

1973

Exchange pseudopotentials, and Model potentials for alkali atoms.

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1. EXCHANGE PSEUDOPOTENTIALS

and

2. MODEL POTENTIALS FOR ALKALI ATOMS

by

ANIL K. PRADHAN

A Thesis

Submitted to the Faculty of Graduate Studies through the Department
of Physics in Partial Fulfillment of the Requirements for
the Degree of Master of Science at the
University of Windsor

Windsor, Ontario

1973

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447892

ACKNOWLEDGEMENTS

I wish to express my gratitude to Dr. W. E. Baylis for his constant guidance throughout the course of this work. Without his immense help and tremendous patience, this work would never have been in existence.

I would also like to thank Dr. V. B. Sheorey and Dr. G. W. F. Drake for many informative and helpful discussions.

I am indebted to the Department of Physics for financial support.

I would also like to thank Ms. Debbe Peltier for patiently typing up the manuscript.

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ABSTRACT

The single configuration Hartree-Fock equations are numerically tedious and time-consuming to solve on account of the exchange term. This is especially the case for heavy atoms and for molecules and solids. The calculations are greatly simplified by the use of a pseudopotential based on the Free Electron Gas (FEG) model to approximate the exact exchange interaction. In the present report several exchange pseudopotentials are discussed and a new non-local interelectronic exchange pseudopotential is presented. The new pseudopotential can simply be added to the one-electron Hartree approximation and it yields results that are consistently better (i.e. closer to Hartree-Fock) than either the Hartree-Fock-Slater method or Lindgren's Hartree-Slater approximation. Several different numerical techniques developed in order to evaluate the different approximations are also discussed.

I. INTRODUCTION

1. Antisymmetry Postulate and the Exchange Effect

From a study of many-electron wave functions¹, Heisenberg² and Dirac³ were led to the postulate of antisymmetry which states that 'the wave function of a many fermion system must change sign when the coordinates of any two particles are interchanged'.[†]

According to the A.S.P. the total wave function for a given fermion system must be antisymmetric. A simple product function does not have this property; however, if we write the wave function as a linear combination of product functions, the result can be made antisymmetric, for example

$$\Psi = \phi_1(1) \phi_2(2) - \phi_1(2) \phi_2(1) = -[\phi_1(2) \phi_2(1) - \phi_1(1) \phi_2(2)] \quad (1)$$

For an N-particle system the antisymmetric total wave function can be written in the form of a 'Slater' determinant, i.e.

$$\Psi = \begin{vmatrix} \phi_1(1) & \dots & \phi_1(N) \\ \vdots & \ddots & \vdots \\ \phi_N(1) & \dots & \phi_N(N) \end{vmatrix} \quad (2)$$

The resulting wave function is clearly antisymmetric.

The Pauli exclusion principle follows directly from this determinantal form: if we have two electrons in the same spin-orbital, then two of the spin-orbitals from the sequence $\phi_1, \phi_2, \dots, \phi_N$ are identical and the total wave function would be zero since the determinant vanishes (i.e. the corresponding state is non-existent) if two of its rows are identical. It is clear that this can happen only when both the electrons have the same spin as otherwise the spin-orbitals will not be identical.

1. J. C. Slater, Phys. Rev. 34: 1293 (1929)

2. W. Heisenberg, Z. Physik, 38: 411 (1926)

3. P.A.M. DIRAC, PROC. ROY. SOC., LONDON, A112: 661 (1926)

[†] Fermions are particles that have non-integral spin and obey Fermi-Dirac Statistics.

It also follows from antisymmetry that in an N-electron system such as an atom or a molecule we can not have two electrons with the same spin, at the same set of spatial coordinates. The probability density of such electron pairs, therefore, falls to zero as the separation between them goes to zero. Thus we can view each electron in an atom, or any other electron system, as being 'avoided' by all other electrons of the same spin. This phenomenon which is known as the Exchange effect follows directly from the antisymmetry of the wave function under exchange.

2. Variational Principle and Hartree, Hartree-Fock Equations

One can approximate the total wave function for a system in many ways. One way is to simply form a straight-forward product of the individual particles represented by their spin-orbitals. A better method is to form an antisymmetrized product (Slater determinant). We then make use of the variational principle by varying each spin-orbital to minimize the total energy such that the product functions or the determinantal wave function formed from the spin-orbitals yields the best possible approximation to the solution of the Sch. Eq. for that system.⁴

If we use a product function and apply the variational principle then we are led to the so-called Hartree approximation whereas the use of an antisymmetrized wave function yields the Hartree-Fock approximation. For the Hartree case we assume the wavefunction to be a product of orthonormalized orbitals $\phi_i(1)$ in terms of which we can write the average energy as:

4. D. R. Hartree, 'The Calculation of Atomic Structures', John Wiley (New York) 1957.

$$\langle H \rangle = \sum_i \int \varphi_i^*(1) f_i \varphi_i(1) dv_1 + \frac{1}{2} \sum_{i,j} \int \varphi_i^*(1) \varphi_j^*(2) g_{ij} \varphi_i(1) \varphi_j(2) dv_1 dv_2 \quad (3)$$

where f_i and g_{ij} are the one-electron and the two-electron operators respectively explicitly given by (atomic units are used throughout):

$$f_i = -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} \quad ; \quad g_{ij} = \frac{1}{r_{ij}}$$

If we set the variation of $\langle H \rangle$ equal to zero subject to the constraint that the $\varphi_i(1)$ remain normalized then we are led⁵ to the Hartree-equations:

$$\left[f_i + \sum_{j \neq i} \int \varphi_j^*(2) g_{ij} \varphi_j(2) dv_2 \right] \varphi_i(1) = -\lambda_i \varphi_i(1) \quad (4)$$

where according to the Koopman's Theorem (Appendix A) ' λ_i ' represents the binding energy ' E_i ' of the i^{th} orbital.

In the Hartree-Fock case we vary the individual $\varphi_{i\lambda}$ to minimize the average energy subject to the condition that all $\varphi_{i\lambda}$ remain normalized and also that any two $\varphi_{i\lambda}$ with the same m_λ value should be orthogonal.

Eq. (3) for the H-F case can be written as:

$$\langle H \rangle = \sum_i \int \varphi_i^*(1) f_i \varphi_i(1) dv_1 + \frac{1}{2} \sum_{i,j} \int \varphi_i^*(1) \varphi_j^*(2) g_{ij} \times [\varphi_i(1) \varphi_j(2) - \delta_{m_{\lambda_i}, m_{\lambda_j}} \varphi_j(1) \varphi_i(2)] dv_1 dv_2 \quad (5)$$

The Kroenecker δ in the second integral (known as the 'exchange integral') makes sure that there is a contribution due to exchange only when

Otherwise the exchange integral is zero. Now if we again apply the variational principle to (5) subject to the normalization constraint, we obtain⁴ the Hartree-Fock equations:

5. J. C. Slater, Th. of Atomic Structure, Vol. II

$$[f_i + \sum_j \int \phi_j^*(2) g_{ij} \phi_j(2) dv_2] \phi_i(1) - \sum_j \delta_{m_i, m_j} X$$

$$\sim \left[\int \phi_j^*(2) g_{ij} \phi_j(2) dv_2 \right] \phi_i(1) = E_i \phi_i(1) \quad (6)$$

E_i , as before represents the binding energy. The Hartree-Fock equations are similar to the Hartree equations (4) except for the third term on the LHS which represents the exchange effect. It is therefore known as the 'exchange term'.

3. The Exchange Term

The first two terms in Eq. (6) represent the kinetic energy plus the electron-nuclear interaction and the electron-electron interaction of the i^{th} electron, represented by ' ϕ_i ' with all others. The exchange term however is multiplied by ϕ_j rather than ϕ_i and therefore its interpretation as some kind of potential representing the exchange interaction is generally consistent only if the potential is nonlocal. Also, it can be seen from Eq. (6) that on account of the exchange term the solution to the H-F equations may be quite involved.

The physical interpretation of the exchange term and a simplified representation for it was first given by Slater⁶ (1952) in the following manner.

First of all the exchange term corrects for the electrostatic interactions of the electron with itself which is included in the second term of Eq. (6) as the summation does not exclude the $i = j$ term. (In the Hartree case the $i = j$ term is omitted hence the self-interaction is

6. J.C. Slater, Phys. Rev., 81, No. 3, 1951.

automatically excluded.) Secondly the exchange term represents the correction to the electrostatic term in the potential due to antisymmetry or exchange whereby the electron in question is avoided by other electrons of the same spin. One can therefore think of each electron as being surrounded by an exchange 'hole' whose density, called the exchange charge density, is minus the total charge density of the given spin less the sum of the probability densities of the electrons of the same spin (which is zero at the position of the electron and increases as we move away from it).

In order to interpret the exchange term quantitatively, Slater rewrote the exchange term (see Eq. (6)) as

$$\sum_j \delta m_{s_i, m_{s_j}} \left[\frac{\int \phi_j^*(2) \phi_i^*(1) \frac{1}{r_{12}} \phi_j(1) \phi_i(2) d\tau_{12}}{\phi_i^*(1) \phi_i(1)} \right] \phi_i(1) \quad (7)$$

This term represents the potential, at the position of the i^{th} electron, due to the exchange charge density

$$\sum_j \delta m_{s_i, m_{s_j}} \left[\frac{\phi_i^*(1) \phi_j^*(2) \phi_j(1) \phi_i(2)}{\phi_i^*(1) \phi_i(1)} \right] \quad (8)$$

located at the position of the j^{th} electron.

Eq. (8) can be simplified by using a weighted mean of the exchange charge density. This should not result in too large an error since we expect that in a system, such as an atom; the exchange charges for different wave functions corresponding to the same spin will not be very different from each other as they reduce to the same value when $(2) \rightarrow (1)$ and also integrate to the same value. Also if the number of electrons of both spins is nearly the same, as is usually the case, then the wave func-

tions of opposite spins will nearly be the same.

The exchange charge density is averaged by means of the weight factor

$$\frac{\varphi_i^*(1) \varphi_i(1)}{\sum_j \varphi_j^*(1) \varphi_j(1)} \quad (9)$$

which is the probability of an electron at (1) to be in state 'i'. Thus using (9) to average over (8) we can rewrite the Hartree-Fock equations (6) in the following simplified manner:

$$\left[f_1 + \sum_{k=1}^N \int \varphi_k^*(2) g_{12} \varphi_k(2) d\tau_2 - \frac{1}{2} \sum_{j=1}^N \sum_{k=1}^N \frac{\int \varphi_j^*(1) \varphi_k^*(2) g_{12} \varphi_k(1) \varphi_j(2) d\tau_2}{\sum_{i=1}^N \varphi_i^*(1) \varphi_i(1)} \delta m_{sj} m_{sk} \right] \times \varphi_i(1) = E_i \varphi_i(1) \quad (10)$$

4. The SCF Method and the Solution of H and H-F Equations

The atomic potential within which each electron is supposed to be bound, consists of terms due both to electron-nuclear attraction to the electrostatic interaction with other electrons in the atom. The atomic potential for the i^{th} electron (without exchange) can therefore be written as:

$$\begin{aligned} V_A^{(i)}(\lambda) &= V_{e_i-n}(\lambda) + \sum_{j \neq i} V_{e_i-e_j}(\lambda - \lambda') \\ &= -\frac{Z}{\lambda_i} \left(1 + \int_0^\infty \frac{\rho^{(i)}(\lambda') d\lambda'}{|\lambda - \lambda'|} \right) \end{aligned} \quad (11)$$

where $\rho^{(i)}(\lambda')$ is the total electronic density excluding the i^{th} electron and is given by

$$\rho^{(i)}(\lambda') = \sum_{j \neq i} \omega_j \rho_j(\lambda') = \sum_{j \neq i} \omega_j |\varphi_j|^2$$

here ' ω_j ' refers to the occupancy number of the j^{th} orbital and ' ϕ_j ', to the corresponding wave function. This is the potential found in the Hartree method.

In the previous section we saw how Slater simplified the H-F equations using the notion of the averaged exchange charge density. If we call this exchange density ' ρ_x ', then the exchange potential due to ' ρ_x ' is given by

$$V_x^{(i)}(\underline{\lambda}) = \int \frac{d^3\lambda' \rho_x^{(i)}(\lambda')}{|\underline{\lambda} - \underline{\lambda}'|} \quad (12)$$

This expression less the self-interaction is to be added to Eq. (11) to account for exchange. The atomic potential for the i^{th} electron is then expressed as

$$V_A^{(i)}(\underline{\lambda}) = -\frac{Z}{\lambda_i} + \int_0^\infty \frac{\rho(\lambda') d\lambda'}{|\underline{\lambda} - \underline{\lambda}'|} - \int \frac{d^3\lambda' \rho_x^{(i)}(\lambda')}{|\underline{\lambda} - \underline{\lambda}'|} \quad (13)$$

Here unlike Eq. (11) $\rho(\lambda') = \sum_j \omega_j \rho_j(\lambda')$ we include the $i = j$ term since this is cancelled by the self-interaction part of the exchange term. The negative sign for the exchange term arises from the antisymmetry of the total wave function and accounts for the fact that the contribution of exchange to the atomic potential is such as to make it more attractive for a given electron. Since all electrons of like spin tend to avoid the electron in question, there is less electrostatic repulsion than there would be if no exchange was taken into account.

We refer to an expression of the form (12) as an 'exchange pseudopotential'.

Eqs. (11) and (13) represent, in general, the atomic potentials for the Hartree and the Hartree-Fock case respectively. In order to solve the Hartree and the Hartree-Fock equations, one makes use of the Self-Consistent Field (SCF) method originally devised by Hartree⁷.

Each electron is assumed to be moving in a central, spherically symmetrical potential field produced by the nucleus and all other electrons. Thus instead of taking into account the instantaneous interaction of an electron with each of the other electrons, one simplifies the problem by assuming the electron is acted on by the averaged charge distribution, $\Psi^*\Psi$, of the other electrons. When summed over all the electrons of the atom, this charge distribution is nearly spherically symmetrical. The potential arising out of this spherically averaged charge distribution will also be spherically symmetrical or, in other words, will represent a central field.

Now since each electron is assumed to move in this averaged potential; the Hartree and the Hartree-Fock equations are reduced to the simple case of a Schroedinger equation with a spherically symmetrical potential. We then solve these equations for ' ϕ_i ' for all orbitals, build up the total charge density from the wave function of the individual orbitals and find the potential arising from this charge density. Then we take a suitable linear combination of this newly found potential and the original potential and plug this back into the original equation. This iterative process is carried on until the requirement of self-consistency is achieved, i.e. the potential in the i^{th} interaction should be the same as in the

7. D. R. Hartree, Proc. Cambridge Phil. Soc., 24, 89, 111, 426 (1928).

($i - 1$)th iteration (to some desired accuracy). The linear combination mentioned above is constructed such as to accelerate the convergence of the iterative process. Through most of the present work, Pratt's iteration scheme⁸ was used (discussed later).

8. G. W. Pratt, Jr., Phys. Rev. 88, 1217 (1952).
G. W. Pratt, Jr., Phys. Rev. 102, 1303 (1956).

II. APPROXIMATIONS FOR EXCHANGE

As noted above the normally employed exchange term accomplishes two things: first, the removal of self-interaction included in the δ -e term of the potential and second, the correction due to its antisymmetry correlation with electrons of the same spin. Thus it can be sub-divided into two parts: the self-interaction (SI) and the inter-electronic interaction (IE). The separation of the exchange term into these two components was first made by Lindgren⁹ who also showed that for atoms the major function of the exchange term is to correct for self-interaction; i.e. the SI part is the dominant part of exchange¹⁰. The contribution due to SI decreases more or less inversely with Z , the atomic number. For small Z (light atoms) the number of electrons is small and therefore the contribution due to interelectronic exchange between electrons is also small and the exchange mainly consists of SI. As the number of electrons increases with Z , the IE part becomes more important in magnitude. This is clearly illustrated below (Fig. 3., Ref. 9).

We can view the exchange charge density ρ_x as being composed of the charge density ρ_{SI} of the electron itself and ρ_{IE} of the other electrons of the same spin. We then have

$$\int \rho_{SI}(\mathbf{r}') d^3\mathbf{r}' = 1 \quad (14)$$

as this is just the integral over the probability density for a single electron, and for the IE part we should have

9. I. Lindgren, Int. Journ. of Quantum Chem., No. 30 (1971).

10. I. Lindgren and K. Schwartz, Phys. Rev. A, Vol. 5, No. 2 (1972).

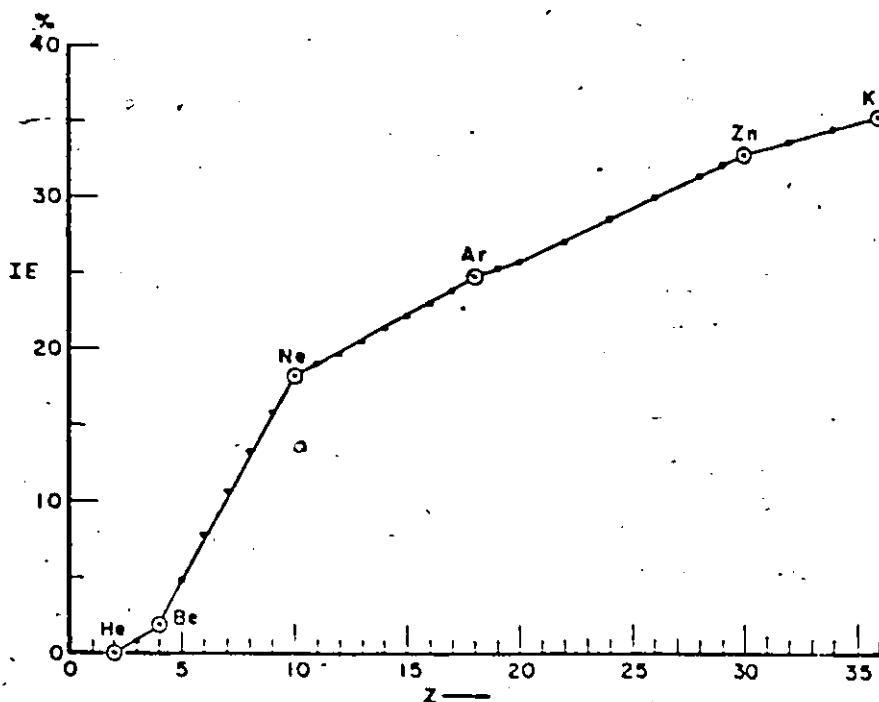


FIG. 3. Magnitude of the interelectronic exchange energy (relative to the total exchange energy) vs atomic number.

(REF. 9.)

$$\int \rho_{IE}^{(i)}(\lambda') d^3 \lambda' = 0$$

(15)

since the probability density of the other like-spin electrons has, due to antisymmetry, merely been redistributed within the system and hence the corresponding net charge is zero.

The total exchange potential (Eq. (12)) can be separated into SI and IE potentials in the following manner (Lindgren and Schwartz, ref. 10).

$$U_{SI}^{(i)}(\lambda) = - \int \frac{\rho_i(\lambda') d^3 \lambda'}{|\lambda - \lambda'|} \quad (16)$$

and

$$U_{IE}^{(i)}(\lambda) = - \frac{1}{\rho_i(\lambda)} \sum_{j \neq i} \delta_{\sigma_i \sigma_j} \int \frac{\varphi_j^*(\lambda) \varphi_j^*(\lambda')}{|\lambda - \lambda'|} \varphi_i(\lambda) \varphi_i(\lambda') d^3 \lambda' \quad (17)$$

where τ refers to the spin orientation. Note that $U_{SI}^{(i)}$ and $U_{IE}^{(i)}$ are non-local in character since they depend on ρ_i or ϕ_i calculated at points other than \underline{r}_i .

We shall now attempt briefly to describe and evaluate several different approximations to exchange.

A. SI Approximations

We first consider the approximations to the SI part of exchange alone. The following three methods are qualitatively and quantitatively compared.

1. Hartree Approximation

This method is the most obvious approach to SI correction: Here we simply omit the summation over the $j = 1$ term (see Eq. (4)) thereby eliminating the SI term (given by Eq. (16)).

In the actual SCF computation this is done by subtracting (16) from the e-e term of the self-consistent atomic potential. For computational purposes, the potential for an orbital i can then be written as:

$$V_i(\underline{r}) = -\frac{Z}{r_i} + \int_0^\infty \frac{\rho_T(r') dr'}{|\underline{r} - \underline{r}'|} - \int_0^\infty \frac{\rho_i(r') dr'}{|\underline{r} - \underline{r}'|} \quad (18)$$

This is the Hartree potential for the given orbital. The Hartree potential is clearly different for each orbital since the SI term corresponding to each orbital is different. This means that the orbitals are eigenstates of slightly different effective atomic potentials and hence the wave functions corresponding to these orbitals are not, in general, orthogonal to one another i.e. we have errors due to overlap.

It is therefore natural to look for a single SI correction to the total effective potential which would be independent of the individual orbitals. The following approximation is one of this type.

2. Amaldi Approximation¹¹

Here we construct the SI correction by calculating the e-e term in the potential from the total electronic density minus the average density of one electron. We have then

$$\rho_x(r') = \rho_{SI}(r') = \frac{1}{Z} \sum_i \omega_i \rho_i(r') = \frac{1}{Z} \rho_T(r') \quad (19)$$

where ρ_T is the total electronic density and ω_i is the occupancy number of the i^{th} orbital.

Then the atomic potential with this average SI correction is:

$$V(\lambda) = -\frac{Z}{\lambda} + \int_0^\infty \frac{\rho_T(r') dr'}{|\lambda - \lambda'|} - \frac{1}{Z} \int_0^\infty \frac{\rho_T(r') dr'}{|\lambda - \lambda'|} \quad (20)$$

Eq. (20) reduces to:

$$V(\lambda) = -\frac{Z}{\lambda} + \left[\int_0^\infty \frac{\rho_T(r') dr'}{|\lambda - \lambda'|} \right] \left[1 - \frac{1}{Z} \right] \quad (21)$$

Eq. (21) is the potential used in the Amaldi approximation.

3. Extended Amaldi Approximation

Another non-local correction which would ensure orthogonality of individual orbitals is obtained by subtracting the average contribution to the e-e term of the total potential by the electron which have the same angular momentum quantum number (since orbitals with different l are automatically orthogonal). This results in the following expression for the potential with SI correction:

11. P. Gombás, 'Pseudopotentiale', Pg. 41, Springer Verlag (New York), 1967.

$$V_e(\lambda) = -\frac{Z}{\lambda} + \int_0^\infty \frac{\rho_T(\lambda') d\lambda'}{\lambda^2 - \lambda'^2} - \frac{\sum_{n,l} \delta_{nl} \int_0^\infty \frac{\rho_{nl}(\lambda') d\lambda'}{\lambda^2 - \lambda'^2}}{\sum_{n,l} \omega_{nl} \delta_{nl}} \quad (22)$$

where ρ_{nl} is the charge density for the orbital n, l . The numerator of the third term is the contribution to the potential by all electrons of a given l and the denominator is the number of such electrons. This potential is clearly different for different l values, but the wave functions derived from this potential are orthogonal.

The three types of SI corrections described above were also studied quantitatively (see Table I, pg. 18) and it was found that the two approximations involving an averaging process over different or all orbitals, are not very good in the sense that the one electron eigenenergies calculated from these potentials are not in good agreement with the Hartree-Fock binding energies as they should be if the exchange has been taken into account properly. The reason for this is as follows. The contribution to the e-e term of the atomic potential by an individual electron varies widely from orbital to orbital. For an electron in 1S orbital, this contribution is larger than that of any other electron in the atom. Due to the absence of any shielding (from the nuclear charge) by other electrons; the removal of a 1S electron can be roughly thought of as being equivalent to adding a +ve charge to the nucleus. Therefore the self-interaction term is largest for the 1S orbital and decreases in magnitude successively for higher orbitals. Clearly, then, if we account for the self-interaction only in an averaged manner, as we did in the last two approximations, we would incur an error for each orbital. The largest errors would be for the

first and the last orbitals since the average is farthest from the extremes. This is indeed found to be the case if we compare the binding energies for the Hartree approximation and the other two approximations (Table I). The Hartree approximation is found to be closest to the H-F and this implies that the error incurred due to the non-orthogonality of the orbitals in this approximation is not as serious as the one made by taking an average value for the self-interaction of different orbitals.

It is clear that the Hartree approximation treats the self-interaction part of the exchange exactly but introduces some error in the wave functions on account of non-orthogonality. We can overcome this problem by orthonormalizing the wave functions while carrying out the SCF calculations. This is done by subtracting the non-orthogonal components of the wave function of other electrons from the wave function of the electron in question (Schmidt orthogonalization). Let i be the index referring to the orbital under consideration and j , the index which refers to all other electrons. Then the orthogonalized wave function Ψ_{i0} can be written in terms of the non-orthogonal, normalized Ψ_i and other already orthonormalized $\Psi_{j'}$ as follows:

$$\Psi_{i0} = \Psi_i - \sum_j |\Psi_j\rangle \langle \Psi_j | \Psi_i\rangle \quad (23)$$

($|\Psi_j\rangle \langle \Psi_j|$ is the complete projection operator onto the $|j\rangle$ space and $\langle \Psi_j | \Psi_j \rangle = 1$). The Ψ_{i0} can then be renormalized to yield the orthonormalized wave function from which we can form the electronic density ρ_i to be used for constructing the self-consistent potential. Orthogonalization need only be performed in the last few iterations of the

SCF calculations. Table I gives the data for the various SI approximation discussed above.

B. Approximations for Total Exchange

In this section we shall discuss several pseudopotentials which approximate the total exchange term. The standard approach is to investigate the exchange charge of a free electron in a uniform free electron gas (FEG) and therefrom devise a pseudopotential for non-uniform cases such as atoms or molecules. The FEG model has been used in solid state physics by F. Bloch to derive an expression for the averaged exchange charge density of an electron¹². Due to the large number of electrons, in solids, the FEG treatment is quite successful in accounting for exchange. The following section discusses the general theory behind the FEG model along with the pseudopotential proposed by Slater (ref. 6). Later sections deal with several other pseudopotentials based on the same general theory.

1. The FEG Model and the Slater Approximation

The first assumption, implicit in the use of the FEG model, is that the electrons in the system under consideration, an atom or a molecule(s), constitutes a completely degenerate free electron gas. According to the Fermi-Dirac statistics, at absolute zero we can put two electrons of opposite spin into a cell in phase space of volume h^3 and the electrons occupy all energy levels, up to the top of the Fermi distribution i.e. to energy levels with the maximum momentum, say P_0 . The volume of phase space occupied by n paired electrons is thus $\frac{n}{2} h^3$ which is a product of the coordinate space volume v and the momentum-space volume

$$\frac{4}{3} \pi P_0^3$$

(24)

12. F. Seitz, 'Modern Theory of Solids', McGraw-Hill (New York), 1940.

TABLE I

Self-Interaction Approximations

One electron eigenvalues (Hartrees)

	AMALDI	EXTENDED AMALDI	HARTREE*	HARTREE (Orthonormalized)	HARTREE- FOCK
Na	1S 36.4347	37.4087	40.6365	40.7178	40.478
	2S 2.0908	2.1475	2.1749	2.1805	2.797
	2P 1.1394	1.1417	1.2243	1.2386	1.518
	3S 0.2246	0.2220	0.1641	0.1646	0.182
Hg	1S 2732.593	2739.424	2775.870	2777.376	2778.639
	2S 455.036	457.024	462.196	463.056	470.734
	2P 433.699	438.461	446.054	447.014	452.176
	3S 106.619	107.195	108.493	108.815	113.136
	3P 98.235	98.886	100.243	100.595	104.341
	3D 82.686	82.472	85.235	85.649	88.145
	4S 22.253	22.623	23.029	23.116	25.573
	4P 18.896	19.187	19.439	19.527	21.699
	4D 12.427	12.339	12.888	12.974	14.610
	4F 3.7097	3.810	4.183	4.251	5.012
	5S 3.3463	3.337	3.468	3.474	4.182
	5P 2.2006	2.273	2.294	2.301	2.851
	5D 0.4487	0.445	0.459	0.4609	0.714
	6S 0.2812	0.2774	0.234	0.2342	0.261

* without orthonormalization

Consequently the density is

$$\rho \equiv \frac{n}{V} = n \frac{\frac{4}{3} \pi p_0^3}{\frac{n}{2} h^3} = \frac{8}{3} \frac{\pi}{h^3} p_0^3 \quad (25)$$

The deBroglie wavelength h/p_0 associated with the maximum momentum can now be expressed as follows:

$$\lambda_{dB} = \frac{h}{p_0} = \left[\frac{8}{3} \frac{\pi}{n} V \right]^{1/3} = \left[\frac{4}{3} \pi \right]^{2/3} r_0 \quad (26)$$

where r_0 is the radius of a spherical volume $\frac{4}{3} \pi r_0^3$ containing one electron of a given spin:

$$r_0 = \left[\frac{3}{4 \pi \rho_\sigma} \right]^{1/3}$$

and where ρ_σ is the density of electrons of same spin.

The exchange potential energy $U_x^{(e)} = U_{SI}^{(e)} + U_{IE}^{(e)}$ for a FEG is calculated from Eqs. (17) and (18) using plane waves for the Φ 's. One finds¹³ (in gaussian cgs units)

$$U_x^{(e)} = e^2 \left[\frac{4 p_0}{h} \right] F(\eta) = e^2 \left[\frac{6}{\pi} \right]^{2/3} \left[\frac{1}{r_0} \right] F(\eta) \quad (27)$$

where $\eta = k/k_F$ and

$$F(\eta) = \frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left[\frac{(1+\eta)}{(1-\eta)} \right] \quad (28)$$

The function $F(\eta)$ goes from unity when $\eta = 0$ for an electron of zero energy, to 1/2 when $\eta = 1$ at the top of the Fermi distribution. It has been shown¹⁴ that if we average over all wave functions then the weighted

13. P.A.M. Dirac, Proc. Cambridge Phil. Soc. 26, 376 (1930).

14. Slater, Ibid.

average of $F(r)$ is $3/4$. Using this value for $F(r)$ in (27) and choosing atomic units by letting $e = 1$ (also $m_e = \hbar = 1$); we obtain the Slater pseudopotential for the exchange potential energy, $V_x^S = \langle U_x^S \rangle$:

$$V_x^S(r) = -\frac{3}{4} \left[\frac{6}{\pi} \right]^{2/3} \frac{1}{r_0} = -3 \left[\frac{3(n/v)}{8\pi} \right]^{1/3} \quad (29)$$

where n/v is interpreted as the local electronic charge density $\rho(r)$ which is a function of position of the electron in question. The Slater approximation is therefore local in character. Explicitly

$$V_x^S(r) = -3 \left[\frac{3}{8\pi} \rho(r) \right]^{1/3} \quad (30)$$

where

$$\rho(r) = \sum_j \phi_j^*(r) \phi_j(r) \quad (31)$$

The summation in Eq. (31) is done over all electrons which means that the Slater pseudopotential includes an approximate SI correction. Using (30) we can rewrite the H-F equation (10) as

$$\int d^3r' \left[\phi_j^*(r') \frac{1}{|r-r'|} \phi_i(r') \right] \phi_i(r) - 3 \left\{ \frac{3}{8\pi} \sum_j \phi_j^*(r) \phi_j(r) \right\}^{1/3} \phi_i(r) = E_i \phi_i(r) \quad (32)$$

The SCF method can now be applied to (32) quite easily by first solving it for each of the wave functions ϕ_i (starting with an initial guess for the part in square brackets), then finding the total charge density due to all ϕ_i 's, then calculating the potential as we described in section I, and reiterating.

2. Exchange Hole and FEG Potentials

In order to derive other possible pseudopotentials for exchange from the results for a FEG, let us now investigate in more detail the exchange energy in a FEG and the concept of an exchange hole. From Eq. (10) it can be seen that the total exchange energy in the Hartree-Fock approximation is given by:

$$E_x = -\frac{1}{2} \int d^3r \int d^3r' \sum_{\sigma} \frac{|p_{\sigma}(r, r')|^2}{|r - r'|} \quad (33)$$

where
$$p_{\sigma}(r, r') = \sum_j \psi_{j\sigma}^*(r) \psi_{j\sigma}(r') \quad (34)$$

and σ refers to the spin orientation.

Now for a FEG confined in volume Ω we can write the one-electron wave functions in terms of plane waves i.e.

$$\psi_j(r) = \frac{1}{\sqrt{\Omega}} e^{i k_j \cdot r} \quad (35)$$

so that (34) becomes:

$$p_{\sigma}(r, r') = \frac{1}{\Omega} \sum_j e^{i k_j \cdot (r - r')} \delta_{\sigma, \sigma_j} \quad (36)$$

For large Ω we approximate $\frac{1}{\Omega} \sum_j$ by the integral $\frac{1}{(2\pi)^3} \int d^3k$; hence

$$p_{\sigma}(r, r') = \frac{1}{(2\pi)^3} \int d^3k e^{i k \cdot (r - r')} \quad (37)$$

Making the transformation $x = \cos \theta$ and integrating up to the Fermi momentum k_F we obtain

$$p_{\sigma}(r, r') = \frac{2\pi}{(2\pi)^3} \int_0^{k_F} k^2 dk \int_{-1}^1 dx e^{i k |r - r'| x} \quad (38)$$

which yields

$$\rho_{\sigma}(\underline{\lambda}, \underline{\lambda}') = \frac{2k_F^3}{(2\pi)^2} \left[\frac{\sin \xi - \xi \cos \xi}{\xi^3} \right] \quad (39)$$

where

$$\xi \equiv k_F |\underline{\lambda} - \underline{\lambda}'|$$

we now define the quantity

$$h(\xi) \equiv \left[3 \left\{ \frac{\sin \xi - \xi \cos \xi}{\xi^3} \right\} \right]^2 \quad (40)$$

which is analogous to the averaged exchange charge density formula for a free electron gas derived by Bloch (see ref. 12).

We now have

$$\rho_{\sigma}(\underline{\lambda}, \underline{\lambda}') = \frac{k_F^3}{6\pi^2} h^{1/2}(\xi) \quad (41)$$

From the previous section we know that the electron density for electrons with a given spin σ in a FEG can be derived directly using phase space concept i.e.

$$\rho_{\sigma}(\underline{\lambda}) = \frac{\rho(\underline{\lambda})}{2} = \frac{4/3 \pi (h k_F)^3}{h^3} = \frac{4}{3} \pi \left[\frac{k_F}{2\pi} \right]^3 \quad (42)$$

where $(2\pi/k_F)$ is the deBroglie wavelength associated with the Fermi momentum. Eq. (41) reduces to this straightforward statistical result as $\underline{\lambda} \rightarrow \underline{\lambda}'$

and $\rho_{\sigma}(\underline{\lambda}, \underline{\lambda}') \rightarrow \rho_{\sigma}(\underline{\lambda})$ i.e.

$$\rho_{\sigma}(\underline{\lambda}, \underline{\lambda}) = \frac{k_F^3}{6\pi^2} = \frac{4}{3} \pi \left[\frac{k_F}{2\pi} \right]^3 \quad (43)$$

since $h(\xi) = 1$ for $\xi = 0$ (see Eq. (40)). Combining (41) and (42) we can write

$$\rho_{\sigma}(\underline{r}, \underline{r}') = \rho_{\sigma}(\underline{r}) h^{\frac{1}{2}}(\xi) \quad (44)$$

and substituting (44) into (33) we obtain

$$E_x = -\frac{1}{2} \int d^3r \sum_{\sigma} \rho_{\sigma}(r) V_x^{FEG}(r) \quad (45)$$

where $V_x^{FEG}(r)$ is the exchange potential due to $\rho_{\sigma}(r')$ at the point r and is given by

$$V_x^{FEG}(r) = k_F \int d^3r' \rho_{\sigma}(r') \frac{h(\xi)}{\xi} \quad (46)$$

For a FEG the density ρ is assumed to be constant, and hence

$$\begin{aligned} V_x^{FEG}(r) &= k_F \rho_{\sigma}(r) \int_{\infty}^{\xi} d\xi \frac{h(\xi)}{\xi} \\ &= \frac{4\pi}{k_F^2} \rho_{\sigma}(r) \int_0^{\infty} d\xi \xi h(\xi) \\ &= \frac{2}{3} \left[\frac{6}{\pi} \rho_{\sigma}(r) \right]^{1/3} \int_0^{\infty} d\xi \xi h(\xi) \end{aligned} \quad (47)$$

where we have used $\xi = k_F |\underline{r} - \underline{r}'|$ and $d\xi = k_F d|\underline{r} - \underline{r}'|$

The value of the integral in Eq. (47) is 9/4 (see Appendix B) so that

$$V_x^{FEG}(r) = \frac{3}{2} \left[\frac{6}{\pi} \rho_{\sigma}(r) \right]^{1/3} \quad (48)$$

The quantities $h(\xi)$ and $|\rho_{\sigma}(\underline{r}, \underline{r}')|^2$ can now be given a physical interpretation in terms of the probability distribution of the electrons. The exchange effect, as noted above, represents the antisymmetry correlation between electrons of the same spin. The probability of an electron being found at r depends on whether or not an electron of the same spin is at

λ' , therefore the actual probability of there two 'dependent' events is:

$$P(\lambda) P(\lambda') - |P(\lambda, \lambda')|^2 \quad (49)$$

where $|P(\lambda, \lambda')|^2$ is due to the antisymmetry correlation between $P(\lambda)$ and $P(\lambda')$ and is given by

$$|P(\lambda, \lambda')|^2 = P(\lambda) P(\lambda') h(\xi) \quad (50)$$

Now the interpretation of $h(\xi)$ is also clear. It represents the 'shape' of the so-called exchange hole associated with the electron at some point λ . The exchange charge density for an electron at λ is simply

$$P_x(\lambda') = P(\lambda') h(\xi) \quad (51)$$

The Slater FEG approximation given above (Eq. (30)) follows immediately if we take

$$P_x(\lambda') = P(\lambda) h(\xi) \quad (52)$$

i.e. to be local. This yields the Slater exchange potential

$$V_x^S(\lambda) = \int \frac{P_x(\lambda') d^3\lambda'}{|\lambda - \lambda'|} = V_x^{FEG}(\lambda) = \frac{3}{2} \left[\frac{6}{\pi} P(\lambda) \right]^{1/3} \quad (53)$$

3. Generalized Exchange Hole Method

In the previous section we considered the exchange hole method with respect to a free electron gas and showed that the Slater approximation follows if we assume the exchange charge density to be local. However, this approximation is valid only when we have a large number of electrons distributed within a system in such a manner that constant density can be

assumed. In general we do not have such uniform homogeneous systems, but rather systems such as light atoms or molecules where the electrons are distributed in shells of widely varying electronic density. In this section, therefore, we shall attempt to generalize the exchange hole method discussed in the previous section.

We rewrite Eqs. (45) and (46) with an exchange hole whose shape is still to be specified i.e.

$$E_x = -\frac{1}{2} \int d^3r \left[\sum_j \rho_{\sigma j}(r) V_x^{j\sigma}(r) \right] \quad (54)$$

where

$$V_x^{j\sigma} = \frac{\int d^3r' \rho_{\sigma j}(r') h(\underline{r}, \underline{r}')}{|\underline{r} - \underline{r}'|} \quad (55)$$

then comparing Eqs. (33) and (54) along with (50) we obtain

$$\frac{\int d^3r' |\rho_{\sigma}(\underline{r}, \underline{r}')|^2}{|\underline{r} - \underline{r}'|} = \rho_{\sigma}(\underline{r}) \frac{\int d^3r' \rho_{\sigma}(r') h(\underline{r}, \underline{r}')}{|\underline{r} - \underline{r}'|} \quad (56)$$

which immediately leads to (from Eq. (34)):

$$\begin{aligned} h(\underline{r}, \underline{r}') &= \frac{|\rho_{\sigma}(\underline{r}, \underline{r}')|^2}{\rho_{\sigma}(\underline{r}) \rho_{\sigma}(\underline{r}')} \\ &= \frac{\sum_{i,j} \phi_{i\sigma}^*(\underline{r}) \phi_{j\sigma}^*(\underline{r}) \phi_{i\sigma}(\underline{r}') \phi_{j\sigma}(\underline{r}')}{\sum_{i,j} \phi_{i\sigma}^*(\underline{r}) \phi_{j\sigma}^*(\underline{r}') \phi_{i\sigma}(\underline{r}') \phi_{j\sigma}(\underline{r})} \end{aligned} \quad (57)$$

This, then, is the expression for the shape of the exchange hole in general.

From (57) one can derive the following properties of $h(\underline{r}, \underline{r}')$:

$$h(\underline{r}, \underline{r}) = 1 \quad (58a)$$

$$h(\underline{r}, \underline{r}') = h(\underline{r}', \underline{r}) \quad (58b)$$

assuming the ϕ_i 's to be orthonormal i.e.

$$\int d^3x \phi_i^*(x) \phi_j(x) = \delta_{ij}$$

we get

$$\int d^3x \phi_\sigma(x) h(x, x') = 1 \quad (58c)$$

Since

$$h(x, x') = \frac{|\phi_\sigma(x, x')|^2}{\phi_\sigma(x) \phi_\sigma(x')}$$

and if we let $\phi_{i\sigma}(x) = X_i$ and $\phi_{i\sigma}(x') = Y_i$ (X_i and Y_i are components of vector \underline{X} and \underline{Y}), then

$$h(x, x') = \frac{|\underline{X} \cdot \underline{Y}|^2}{|\underline{X}|^2 |\underline{Y}|^2}$$

which from Schwartz's inequality leads to

$$h(x, x') \leq 1 \quad (58d)$$

and also that 'h' is positive definite i.e.

$$h(x, x') \geq 0 \quad (58e)$$

Next we consider the limiting cases.

1. One Electron Case: If we have only one electron with some spin ' σ ',

(57) reduces to

$$h(x, x') = 1 \quad (59)$$

which, recalling Eq. (58c) might be extended to N_σ electron of spin ' σ ' by

$$h(x, x') = \frac{1}{N_\sigma} \quad (60)$$

Since we know that the exchange charge density (51) can be given generally in terms of h as:

$$\rho_x(\lambda, \lambda') = \rho_\sigma(\lambda') h(\lambda, \lambda') \quad (61)$$

We can use (60) with (51) to obtain

$$\rho_x(\lambda, \lambda') = \frac{1}{N_\sigma} \rho_\sigma(\lambda') \quad (62)$$

a variant of the Amaldi approximation discussed above.

2. High or Constant Density Limit: The radius of the exchange hole has the dimension of $\rho_\sigma^{-1/3}$, therefore in the high density limit, when ρ_σ is practically constant, we can assume that within the region of dimension λ_0

we have

$$\left| \frac{\delta \rho_\sigma / \delta \lambda}{\rho_\sigma} \right| \rho_\sigma^{-1/3} = \left| \frac{\delta \rho_\sigma}{\delta \lambda} \right| \rho_\sigma^{-4/3} \ll 1 \quad (63)$$

Then in Eq. (55) we can approximately evaluate $\rho_\sigma(\lambda')$ at $\lambda' = \lambda$ i.e. substitute for $\rho_\sigma(\lambda')$ by $\rho_\sigma(\lambda)$ yielding:

$$V_x(\lambda) \cong \rho_\sigma(\lambda) \int \frac{d\lambda' h(\lambda, \lambda')}{|\lambda - \lambda'|} \quad (64)$$

(64) is a local approximation for the exchange potential. As mentioned before $h(\lambda, \lambda')$ can be determined from a FEG model. In the Slater approximation¹⁵

$$h(\lambda, \lambda') = 1 \quad \text{for } |\lambda - \lambda'| < \lambda_0 \equiv \left[\frac{3}{4\pi \rho_\sigma} \right]^{1/3} \\ = 0 \quad \text{for } |\lambda - \lambda'| > \lambda_0 \quad (65)$$

λ_0 is sometimes called the radius of the exchange hole!

15. Slater, Ibid.

C. Interelectronic Exchange

As noted above, in the FEG model, it is assumed that the number of electrons is large. If this is not the case then the derivation of various expressions based on the FEG model is not completely justified. For small systems like light atoms, the error introduced thereby might be appreciable. Recall that the exchange term contains two parts--SI (self-interaction) and IE (interelectronic interaction) due to all other electrons. Lindgren¹⁶ has shown that for small electronic systems it is advantageous to consider these two parts separately since the SI is not negligible as it is in the FEG case. The ratio of SI to IE contributions is simply of the order of

$$\frac{V_{SI}^{FEG}}{V_{IE}^{FEG}} \sim N_{\sigma}^{-1/3} \quad (66)$$

where N_{σ} is the number of electrons of spin σ . From (66) it is obvious that for large systems where N_{σ} is large the contribution to the exchange potential due to SI might be negligible.

However, for small systems where this is not the case, it is advantageous to treat the SI and IE terms separately because the SI term can be treated exactly without any approximation as we did in the Hartree case (section A) where we simply subtracted the contribution to the e-e term of the atomic potential by the electron in question. After this exact treatment for the SI we are left with the task of finding a pseudopotential to approximate the IE term alone i.e. find an interelectronic exchange pseudopotential.

16, see ref. 9

Specifically, we consider the HF matrix elements of the inter-electronic interaction term i.e.

$$\frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \left[\langle ij | \lambda_{ij}^{-1} | ij \rangle - \langle ij | \lambda_{ij}^{-1} | ji \rangle \right] \quad (67)$$

where the first part represents direct e.s. interaction and the second part represents exchange. In integral notation we have:

$$\begin{aligned} & \frac{1}{2} \int d^3\lambda_1 \int d^3\lambda_2 \sum_{\substack{i,j \\ i \neq j}} \lambda_{ij}^{-1} \left[|\varphi_i(\mathbf{r}_1)|^2 |\varphi_j(\mathbf{r}_2)|^2 - \varphi_i^*(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \varphi_j^*(\mathbf{r}_1) \varphi_i(\mathbf{r}_2) \delta_{\mathbf{r}_1, \mathbf{r}_2} \right] \\ &= \frac{1}{2} \int d^3\lambda_1 \sum_i |\varphi_i(\mathbf{r}_1)|^2 \left[\int d^3\lambda_2 \lambda_{ij}^{-1} \sum_{\substack{j \\ i \neq j}} \left[|\varphi_j(\mathbf{r}_2)|^2 - \frac{\varphi_j(\mathbf{r}_2) \varphi_j^*(\mathbf{r}_1) \varphi_i(\mathbf{r}_1)}{\varphi_i(\mathbf{r}_1)} \delta_{\mathbf{r}_1, \mathbf{r}_2} \right] \right] \\ &= \frac{1}{2} \int d^3\lambda_1 \sum_i |\varphi_i(\mathbf{r}_1)|^2 \left[\int d^3\lambda_2 \lambda_{ij}^{-1} \left\{ \rho(\mathbf{r}_2) - \frac{\rho(\mathbf{r}_2)}{\rho(\mathbf{r}_1)} \right\} - V_{IE}^{(i)}(\mathbf{r}_1) \right] \end{aligned} \quad (68)$$

where we have introduced the interelectronic exchange potential given by:

$$V_{IE}^{(i)}(\mathbf{r}_1) = \int d^3\lambda_2 \lambda_{ij}^{-1} \frac{\varphi_i(\mathbf{r}_2)}{\varphi_i(\mathbf{r}_1)} \sum_j \varphi_j^*(\mathbf{r}_2) \varphi_j(\mathbf{r}_1) \delta_{\mathbf{r}_1, \mathbf{r}_2} \quad (69)$$

In a manner analogous to that in section B we can rewrite (69) in terms of an interelectronic exchange charge density ρ_{IE} and a factor representing the exchange hole

$$V_{IE}^{(i)}(\mathbf{r}_1) = \int d^3\lambda_2 \lambda_{ij}^{-1} \rho_{IE}^{(i)}(\mathbf{r}_1, \mathbf{r}_2) \quad (70)$$

where, analogous to (51)

$$\rho_{IE}^{(i)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho(\mathbf{r}_2)}{\rho(\mathbf{r}_1)} f^{(i)}(\mathbf{r}_1, \mathbf{r}_2) \quad (71)$$

From (69) then, we can put

$$f^{(i)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\varphi_i(\mathbf{r}_2)}{\varphi_i(\mathbf{r}_1)} \left[\frac{\rho(\mathbf{r}_2, \mathbf{r}_1) - \varphi_i^*(\mathbf{r}_2) \varphi_i(\mathbf{r}_1)}{\rho(\mathbf{r}_2)} \right] \quad (72)$$

where

$$\rho_{\sigma}(2,1) = \sum_i q_{i\sigma}^*(2) \phi_{i\sigma}(1)$$

Now we are looking for an expression for the exchange hole which is composed of the interelectronic charge density alone i.e.

$$\rho_{IE}^{(i)}(\lambda') = \rho_{\sigma}^{TOTAL}(\lambda') - \rho_{\sigma}^{(i)}(\lambda') \quad (73)$$

We therefore construct this expression, say $g^{(i)}(\lambda_1, \lambda_2)$, using (72) and (73), as

$$\begin{aligned} g^{(i)}(\lambda_1, \lambda_2) &= \left[\frac{\rho_{\sigma}(2) - \rho_{i\sigma}(2)}{\rho_{\sigma}(2)} \right] \rho_{i\sigma}^{(i)}(\lambda_1, \lambda_2) \\ &= \frac{\rho_{i\sigma}(1,2) [\rho_{\sigma}(2,1) - \rho_{i\sigma}(2,1)]}{\rho_{i\sigma}(1) [\rho_{\sigma}(2) - \rho_{i\sigma}(2)]} \end{aligned} \quad (74)$$

where

$$\rho_{i\sigma}(2,1) = \rho_{i\sigma}^*(1,2) = q_{i\sigma}^*(2) \phi_{i\sigma}(1)$$

IN TERMS OF WHICH

$$\begin{aligned} \rho_{\sigma}(2,1) &\equiv \sum_i \phi_{i\sigma}(2) \phi_{i\sigma}(1) \\ \rho_{i\sigma}(1) &\equiv \rho_{i\sigma}(1,1) \\ \rho_{\sigma}(1) &\equiv \rho_{\sigma}(1,1) \end{aligned} \quad (75)$$

It follows immediately that

$$\begin{aligned} \rho_{i\sigma}(1,2) \rho_{i\sigma}(2,1) &= \rho_{i\sigma}(1) \rho_{i\sigma}(2) \\ \int d^3\lambda_2 \rho_{i\sigma}(1,2) \rho_{i\sigma}(2,1) &= \int d^3\lambda_2 \rho_{i\sigma}(1,2) \rho_{i\sigma}(2,1) \\ &= \rho_{i\sigma}(1) \end{aligned} \quad (76)$$

Clearly the expression for the interelectronic exchange hole, $g^{(i)}(\lambda_1, \lambda_2)$ has the following properties

$$g^{(i)}(\lambda_1, \lambda_1) = 1 \quad (77a)$$

and

$$\int d^3\lambda_2 [\rho_{\sigma}(2) - \rho_{i\sigma}(2)] g^{(i)}(1,2) = 0 \quad (77b)$$

Eqs. (71) and (74) combine to give

$$\rho_{IE}^{(u)}(\underline{\lambda}_1, \underline{\lambda}_2) = [\rho_{\sigma}(\underline{\lambda}_2) - \rho_{\sigma}^{(u)}(\underline{\lambda}_2)] g^{(u)}(\underline{\lambda}_1, \underline{\lambda}_2) \quad (78)$$

From (78) we easily obtain the expression for the interelectronic exchange potential

$$V_{IE}^{(u)}(\underline{\lambda}_1) = \int d^3\lambda_2 \frac{\rho_{IE}^{(u)}(\underline{\lambda}_1, \underline{\lambda}_2)}{|\underline{\lambda}_1 - \underline{\lambda}_2|} \quad (79)$$

We can now make use of the FEG model to derive an analytic approximation

for $g^{(u)}(\underline{\lambda}_1, \underline{\lambda}_2)$. From Eq. (35),

$$\begin{aligned} \rho_{\sigma}(\underline{\lambda}, \underline{\lambda}') &= \frac{1}{(2\pi)^3} \int d^3k e^{i\mathbf{k} \cdot \underline{\lambda}_{12}} \\ &= \rho_{\sigma}(\underline{\lambda}_1) h^{\frac{1}{2}}(k_F \lambda_{12}) \end{aligned}$$

$$\rho_{\sigma}(\underline{\lambda}_1, \underline{\lambda}_2) = \frac{1}{\Omega} e^{i\mathbf{k} \cdot \underline{\lambda}_{12}} \rho_{\sigma}(\underline{\lambda}_1) e^{i\mathbf{k} \cdot \underline{\lambda}_{12}}$$

and

$$\rho_{\sigma}(\underline{\lambda}_1) = \frac{\rho_{\sigma}(\underline{\lambda}_1)}{N_{\sigma}} \quad (80)$$

Therefore

$$\begin{aligned} g_{FEG}^{(u)}(\underline{\lambda}_1, \underline{\lambda}_2) &= e^{i\mathbf{k} \cdot \underline{\lambda}_{12}} \left[\frac{h^{\frac{1}{2}}(k_F \lambda_{12}) - N_{\sigma}^{-1} e^{-i\mathbf{k} \cdot \underline{\lambda}_{12}}}{1 - N_{\sigma}^{-1}} \right] \\ &= \left[\frac{e^{i\mathbf{k} \cdot \underline{\lambda}_{12}} h^{\frac{1}{2}}(k_F \lambda_{12}) - N_{\sigma}^{-1}}{1 - N_{\sigma}^{-1}} \right] \quad (81) \end{aligned}$$

where $h^{\frac{1}{2}}(\xi) = -\frac{3}{\xi} \frac{d}{d\xi} j_0(\xi)$ (see Eq. (35) and Appendix I). For a

FEG, then, the IE exchange potential (79) becomes,

$$\begin{aligned} V_{FEG}^{(u)}(\underline{\lambda}_1) &= \int d^3\lambda_2 \frac{[\rho_{\sigma}(\underline{\lambda}_1) - \rho_{\sigma}^{(u)}(\underline{\lambda}_2)]}{|\underline{\lambda}_1 - \underline{\lambda}_2|} g_{FEG}^{(u)}(\underline{\lambda}_1, \underline{\lambda}_2) \\ &= \int d^3\lambda_2 \frac{\rho_{\sigma}(\underline{\lambda}_2)}{|\underline{\lambda}_1 - \underline{\lambda}_2|} \left[e^{i\mathbf{k} \cdot \underline{\lambda}_{12}} h^{\frac{1}{2}}(k_F \lambda_{12}) - N_{\sigma}^{-1} \right] \quad (82) \end{aligned}$$

$$= 4\pi \rho_{\sigma}(\underline{\lambda}_1) \int_0^{\infty} d\lambda_{12} \lambda_{12} \left[\frac{\sin \xi}{\xi} \right] \left[\frac{\sin \xi_F - \xi_F \cos \xi_F}{\xi_F^3} \right] - \int d^3\lambda_2 \frac{\rho_{\sigma}(\underline{\lambda}_2)/N_{\sigma}}{|\underline{\lambda}_1 - \underline{\lambda}_2|}$$

where $\xi = k\lambda_{12}$ and $\xi_F = k_F \lambda_{12}$ (k_F - Fermi Momentum). We have made

use of the following relation

$$\frac{1}{4\pi} \int_{4\pi} d\hat{\lambda}_{12} e^{i\mathbf{k} \cdot \hat{\lambda}_{12}} = \frac{\sin k\lambda_{12}}{k\lambda_{12}} \quad (83)$$

Now since in a FEG,

$$\rho_{\sigma}(\lambda_1) = \rho_{\sigma}(\lambda_2) = \frac{k_F^3}{6\pi^2} \quad (\text{see Eq. (43)})$$

and

$$j_0(\xi) = \sin \xi / \xi$$

$$j_1(\xi) = [\sin \xi - \xi \cos \xi] / \xi^2$$

We have, then, from Eq. (82),

$$V_{\text{FEG}}^{(u)}(\lambda_1) = \frac{2}{\pi} k_F^2 \int_0^{\infty} d\lambda_{12} j_0(k\lambda_{12}) j_1(k_F\lambda_{12}) - \int d^3\lambda_{12} \frac{\rho_{\sigma}(\lambda_2)/N_{\sigma}}{\lambda_{12}} \quad (84)$$

It can be shown that (see Appendix F)

$$\int_0^{\infty} d\lambda j_1(k_F\lambda) j_0(k\lambda) = \frac{k_F^2 - k^2}{4k_F^2 k} \ln \left| \frac{k_F + k}{k_F - k} \right| + \frac{1}{2k_F}$$

therefore after averaging over k , we find that

$$V_{\text{FEG}}^{(u)}(\lambda_1) = \frac{3}{2} \left[\frac{6}{\pi} \rho_{\sigma}(\lambda_1) \right]^{1/3} - \int d^3\lambda_2 \frac{\rho_{\sigma}(\lambda_2)/N_{\sigma}}{\lambda_{12}} \quad (85)$$

The second term on the RHS in (85) clearly represents the self-interaction and the first term is the total (IE + SI) exchange contribution. The first term is identical with the Slater exchange potential (28).

The problem now is to evaluate the second term in Eq. (85). This can be solved in a variety of ways. Two different approaches are discussed below.

1. The Local Interelectronic (LIE) Approximation

We assume constant charge density ρ_i over a spherical region of radius ' r_0 ', such that $\frac{4}{3}\pi r_0^3 \rho_i = 1$. The potential, then, is

$$V_{LIE}^{(i)}(\lambda) = [4\pi \rho_0]^2 \int_0^{\lambda_0} d\lambda \lambda^2 \int_0^{\lambda_0} \frac{d\lambda' \lambda'^2}{\lambda_{>}} \quad (86)$$

where $\lambda_{>}$ is the greater of λ or λ' and r_0 . Now letting $\lambda = \lambda_0 x$ and $\lambda' = \lambda_0 x'$

$$\begin{aligned} V_{LIE}^{(i)}(\lambda) &= \frac{[4\pi \rho_0 \lambda_0^3]^2}{\lambda_0} \int_0^1 dx x^2 \left[\int_0^x dx' \frac{x'^2}{x} + \int_x^1 dx' x' \right] \\ &= \frac{9}{\lambda_0} \int_0^1 dx x \left[\frac{x^3}{3} + \frac{x}{2} - \frac{x^3}{2} \right] \\ &= \frac{6}{5} \left[\frac{4}{3} \pi \rho_0 (\lambda) \right]^{1/3} \\ &= \frac{12}{5} \left[\frac{\pi}{6} \right]^{2/3} \left[\frac{6}{\pi} \rho_0 (\lambda) \right]^{1/3} \end{aligned} \quad (87)$$

In the LIE, then, Eq. (85), the interelectronic exchange pseudopotential can be written as

$$V_{IEFEG}^{(i)}(\lambda) = \left[\frac{6}{\pi} \right]^{1/3} \left[\frac{3}{2} \rho_0 (\lambda)^{1/3} - \frac{12}{5} \left(\frac{\pi}{6} \right)^{2/3} \rho_0 (\lambda)^{1/3} \right] \quad (88)$$

2. Hartree-Slater Approximation

From Eq. (78), ρ_{IE} is zero when $\rho = \rho_0$. Simply making use of this fact we can write down

$$\int d^3x_2 \frac{\rho_0(2)/N}{\lambda_{12}} = \frac{3}{2} \left[\frac{6}{\pi} \rho_0 \right]^{1/3} \quad (89)$$

whereby

$$V_{FEG}^{(i)}(\lambda) = \frac{3}{2} \left[\frac{6}{\pi} \right]^{1/3} \left[\rho_0 (\lambda)^{1/3} - \rho_0 (\lambda)^{1/3} \right] \quad (90)$$

This is the Lindgren's 'Hartree-Slater' approximation (discussed in more detail below).

3. The Present Non-Local Interelectronic Approximation

As noted before there are a variety of ways of using the FEG model

to arrive at an exchange pseudopotential. The present approximation is based directly on the interelectronic exchange hole concept with its representation, $g^{(i)}(\underline{\lambda}_1, \underline{\lambda}_2)$, as given earlier (Eq. (74) and (78)). We write the $V_{\text{IEFEG}}^{(i)}(\underline{\lambda}_1)$ in the following manner:

$$V_{\text{IEFEG}}^{(i)}(\underline{\lambda}_1) = \left[\rho_{\sigma}(\underline{\lambda}_1) - \rho_{\pi}(\underline{\lambda}_1) \right] \int d^3\lambda_2 \frac{g^{(i)}(\underline{\lambda}_1, \underline{\lambda}_2)}{\lambda_{12}} \quad (91)$$

The expression in brackets represents the interelectronic charge density (excluding SI) and the integral over the exchange hole $g^{(i)}(\underline{\lambda}_1, \underline{\lambda}_2)$ represents the antisymmetry correlation factor. The exchange pseudopotential (91) is non-local in character on account of this factor. This is what one expects since the exchange effect itself is non-local.

Once again we refer to the FEG model in order to approximate (91).

Using (80) and (81)

$$\begin{aligned} V_{\text{IEFEG}}^{(i)}(\underline{\lambda}_1) &= \left[\frac{\rho_{\sigma}(\underline{\lambda}_1) - \rho_{\pi}(\underline{\lambda}_1)}{1 - N_{\sigma}^{-1}} \right] \int d^3\lambda_{12} \frac{1}{\lambda_{12}} \left[e^{i\mathbf{k} \cdot \underline{\lambda}_{12}} h^{\frac{1}{2}}(k_F \lambda_{12}) - N_{\sigma}^{-1} \right] \\ &= \left[\frac{\rho_{\sigma}(\underline{\lambda}_1) - \rho_{\pi}(\underline{\lambda}_1)}{1 - N_{\sigma}^{-1}} \right] \left[\frac{3}{2} \left(\frac{6}{\pi} \rho_{\sigma}^2(\underline{\lambda}_1) \right)^{1/3} - \frac{1}{N_{\sigma}} \right] \int d^3\lambda_{12} \frac{1}{\lambda_{12}} \\ &= \frac{3}{2} \left[\rho_{\sigma}(\underline{\lambda}_1) - \rho_{\pi}(\underline{\lambda}_1) \right] \left[\frac{1 - N_{\sigma}^{-1/3}}{1 - N_{\sigma}^{-1}} \right] \left[\frac{6}{\pi} \rho_{\sigma}(\underline{\lambda}_1)^{-2/3} \right] \end{aligned} \quad (92)$$

The numerical factor (second bracket) was chosen so that in the limit when $N_{\sigma} \rightarrow 1$ and hence $\rho_{\sigma} \rightarrow \rho_{\pi}$, $g^{(i)}(\underline{\lambda}_1, \underline{\lambda}_2)$ remains finite. Eq. (92) fits the exchange hole concept more clearly than any of the other approximations since the exchange potential is obtained directly by integrating over the so-called 'exchange hole' $g^{(i)}(\underline{\lambda}_1, \underline{\lambda}_2)$. Hence we expect Eq. (92) to be a

better approximation to Hartree-Fock than other approximations discussed earlier.

The factor $3/2$ in (92) drops out when we apply the Kohn and Sham correction¹⁷ which arises if we vary the one-electron orbitals so as to minimize the total energy: $U_{K-S} = \frac{2}{3} V_{IEFG}$

17. W. Kohn and L. J. Sham, Phys. Rev., 140, 4A, 1133, (1965).

III. COMPUTATIONAL METHODS

1. Self-Consistent Potential

The calculations for the different exchange pseudopotentials were carried out by modifying the Hartree-Fock-Slater Self-Consistent-Field Program written by J. P. Desclaux¹⁸. First we shall describe briefly the numerical procedure used by Desclaux together with the modification that we made.

The radial H-F-S equations for an atom or ion can be written as:

$$\frac{d^2 R_{nl}}{d\lambda^2} = \left[2V_{\text{HFS}}(\lambda) - \epsilon_{nl} + \frac{l(l+1)}{\lambda^2} \right] R_{nl}(\lambda) \quad (93)$$

where the radial wave function is normalized as:

$$\int_0^\infty |R_{nl}|^2 d\lambda = 1 \quad (94)$$

and

$$V_{\text{HFS}}(\lambda) = \frac{1}{\lambda} \left[-Z + \int_0^\lambda \rho(\lambda') d\lambda' + \lambda \int_\lambda^\infty \frac{\rho(\lambda')}{\lambda'} d\lambda' - \lambda \left\{ \frac{81}{32\pi^2} \frac{\rho(\lambda)}{\lambda^2} \right\}^{1/3} \right] \quad (95)$$

The spherically averaged total electronic density $\rho(\lambda)$ is:

$$\rho(\lambda) = \sum_{n,l} \omega_{nl} |R_{nl}|^2 \quad (96)$$

ω_{nl} is the occupation number of the orbital n,l . The last term in Eq. (95) is the Slater exchange pseudopotential given by Eq. (30). Since the free electron exchange approximation does not properly treat the self-consistent Coulomb potential at large r , Latter's correction¹⁹ is applied to (95) i.e.

18. J. P. Desclaux, *Compt. Phys. Commun.* **1** (1969) 216-222.

19. R. Latter, *Phys. Rev.*, **99** (1955) 510.

$$V_{\text{HFS}}(\lambda) = -\frac{(Z-N+1)}{\lambda} \quad \text{if } V(\lambda) \leq -\frac{(Z-N+1)}{\lambda} \quad (97)$$

$$= (95) \quad \text{otherwise}$$

'N' is the total number of electrons. Latter's correction is omitted for cases where the self-interaction is subtracted separately.

In order that our integration mesh may have small 'r' spacing near the origin (nucleus) and large 'r' spacing at large 'r'; we used a log grid.

$$\log \lambda_n - \log \lambda_{n-1} = h$$

$$\text{i.e. } \lambda_n = \lambda_{n-1} e^h \quad (98)$$

If we let $y_n = \ln \lambda_n$ then we have a mesh of equally spaced points ($y_n - y_{n-1} = h$) in 'log r' space. This enables us to use the Numerov method after we transform the radial Schroedinger equation (93) into 'y' grid, by letting:

$$P_{n\ell}(\lambda) = \lambda^{-1/2} R_{n\ell}(\lambda) \quad (99)$$

into (see Appendix C):

$$\frac{d^2 P_{n\ell}}{dy^2} = \lambda^2 \left[2(V(\lambda) - E) + \frac{(\ell + \frac{1}{2})^2}{\lambda^2} \right] P_{n\ell} \quad (100)$$

From the radial wave functions obtained from solving Eq. (100) and using Eq. (99), we calculate the total electronic charge density $\sum_{n,\ell} 4\pi \lambda^2 |R_{n\ell}|^2$, and use this to compute the self-consistent potential (see Note on SCF method, Section 4) through successive iterations.

The Convergence Criterion used in the HFS program is derived from the Pratt Construction scheme²⁰. Given the final value of the potential $V_f^n(\lambda)$ for the n^{th} iteration, the initial value for the next

20. G. W. Pratt, Jr., Phys. Rev. 88, 1217 (1952).

iteration is given by:

$$V_i^{n+1}(\lambda) = \alpha(\lambda) V_i^n(\lambda) + [1 - \alpha(\lambda)] V_f^n(\lambda) \quad (101)$$

writing:

$$\gamma_i(\lambda) = \frac{V_f^n(\lambda) - V_f^{n-1}(\lambda)}{V_i^{n-1}(\lambda) + V_f^n(\lambda) - V_i^n(\lambda) - V_f^{n-1}(\lambda)} \quad (102)$$

Then we impose the following requirements (which may be varied according to the nature of the problem):

$$\begin{aligned} \alpha(\lambda) &= \gamma_i(\lambda) & \text{if } 0 \leq \gamma_i(\lambda) \leq 0.5 \\ \alpha(\lambda) &= 0.5 & \text{if } \gamma_i(\lambda) > 0.5 \\ \alpha(\lambda) &= 0 & \text{if } \gamma_i(\lambda) < 0 \end{aligned} \quad (103)$$

2. Total Energy

The total energy of the atom (including exchange) is given by:

$$E_T = \sum_i \epsilon_i - \frac{1}{2} \sum_{i,j} [V_{e_i - e_j} - E_{ij}^x] \quad (105)$$

where ϵ_i is the eigenvalue of the one-electron hamiltonian:

$$H_i = -\frac{\nabla_i^2}{2} - \frac{Z}{\lambda_i} + \sum_j \left[\langle i,j | \frac{1}{\lambda_{ij}} | i,j \rangle - \langle i,j | \frac{P_{ij}}{\lambda_{ij}} | i,j \rangle \right] \quad (106)$$

The last term on RHS represents the (direct e.s. + exchange) interaction.

The term $\sum_{i,j} V_{e_i - e_j}$ in (105) is the e.s. energy between electrons and is given by:

$$\sum_{i,j} V_{e_i - e_j}(\lambda) = \int_0^\infty \rho_i(u) \left\{ \frac{1}{\lambda} \int_0^\lambda \rho_j(u') du' + \int_\lambda^\infty \frac{\rho_j(u')}{\lambda'} du' \right\} d\lambda \quad (107)$$

Spherically symmetric charge distribution, appropriate for filled subshells, is assumed i.e.

$$\frac{1}{\lambda_{ij}} = \frac{1}{|\lambda_i - \lambda_j|} = \sum_{l=0}^{\infty} \frac{\lambda_{<}^l}{\lambda_{>}^{l+1}} P_l(\cos \theta) \xrightarrow{l=0} \frac{1}{\lambda_{>}} \quad (108)$$

The term E_{ij}^x represents the exchange energy and in general is given by

$$E_{ij}^x = \int_0^\infty \rho_i(\lambda) V_x(\lambda) d\lambda \quad (109)$$

where $V_x(\lambda)$ is the exchange potential.

Now if the final self-consistent atomic potential is $V(\lambda)$ then the total energy can be calculated from the following expression:

$$E_T = \left[\sum_i \epsilon_i - \frac{1}{2} Z \int_0^\infty \frac{\rho_i(\lambda)}{\lambda} d\lambda \right] - \frac{1}{2} \int_0^\infty \rho_i(\lambda) V(\lambda) d\lambda \quad (111)$$

since the effective potential might be slightly different for different orbitals; the calculations are carried out for each orbital using:

$$E_T = \sum_i \left\{ \left[\epsilon_i - \frac{1}{2} Z \int_0^\infty \frac{\rho_i(\lambda)}{\lambda} d\lambda \right] - \frac{1}{2} \int_0^\infty \rho_i(\lambda) V_i(\lambda) d\lambda \right\} \quad (112)$$

where ρ_i is now $|\psi_i|^2$.

3. One-Electron Eigenvalues

The one-electron eigenvalues are calculated using the Eigenvalue Correction Procedure derived by Cooley²¹ (also discussed by Zare and Cashion²²). The procedure is designed to calculate the eigenvalue E and the eigenfunction P of the second order differential equation

$$\frac{d^2 P}{d\lambda^2} = (V - E) P \quad (113)$$

where $V(\lambda)$ is the given potential.

21. J. W. Cooley, Math. of Computation, XV, 363 (1961).

22. R. N. Zare and J. K. Cashion, U. of California, Lawrence Radiation Laboratory, Berkeley, California (1963).

A solution of (113) can be obtained from the Numerov integration formula

$$-Y_{i-1} + 2Y_i - Y_{i+1} + h^2[V_i - E_i]P_i = 0 \quad (114)$$

where

$$Y_i = [1 - (h^2/12)(V_i - E_i)] P_i$$

Equation (114) is used to integrate inward from ∞ , with a first estimate of E_1 , upto the point η_m where $|P_m| \leq |P_{m+1}|$. Then we integrate outward from 0 to η_m and use the Newton Raphson method for calculating the zero of the function (see Eq. (114))

$$F(E) = -Y_{m-1} + 2Y_m - Y_{m+1} + h^2[V_m - E_i]P_m \quad (115)$$

which indicates the amount by which Eq. (114) is not satisfied. We then calculate the desired change in E_1 by

$$\Delta E_i = \frac{[0 - F(E)]}{F'(E)} \quad (116)$$

We add this to original E_1 and repeat the procedure until $\Delta E_1 < \xi =$ some small number. (ξ was taken to be 5×10^{-6} .)

4. Electron Binding Energies

In the case of statistical exchange approximations, like the ones under consideration in this report, the one-electron eigenenergies

E_i are not exactly the same as the corresponding electron binding E_i energies since Koopman's theorem (see Appendix A) is valid only for Hartree-Fock configurations.

In order to circumvent this problem, we calculate the binding energies straightforwardly from the wave functions obtained from the given

potential (containing the statistical exchange approximation e.g. H-S or the present one).

The binding energies in the H-F configuration are given by:

$$E_i = -\langle i | f_1 | i \rangle + \sum_j \langle ij | g_{12} (1 - P_{12}) | ij \rangle \quad (117)$$

where f_1 and g_{12} are the one- and two-electron operators respectively, in the many electron hamiltonian, Eq. (105), and P_{12} is the exchange operator.

Eq. (114) reduces to the following computational form (see Appendix D):

$$\begin{aligned} -E_i &= \int_0^\infty |R_i|^2 \left[E_i - V_i(r) - \frac{Z}{r} \right] dr + \\ &\sum_j \left\{ \omega_j \left[\int_0^\infty dr_1 \int_0^\infty dr_2 \frac{1}{r_{12}} |R_i(r_1)|^2 |R_i(r_2)|^2 \right] + \right. \\ &\sum_l \left[2 \int_0^\infty dr_1 \int_0^\infty dr_2 \frac{r_2^l}{r_{12}^{l+1}} R_i(r_1) R_i(r_2) R_j(r_1) R_j(r_2) \right] \times \\ &\left. [1 < l_j, 0 | l_i, 0; l, 0 > |^2] \right\} \quad (118) \end{aligned}$$

$\omega_j = (2l_j + 1)2$. The Clebsch-Gordon coefficients in (117) are calculated in Appendix E.

IV. RESULTS

In order to judge and compare the effectiveness of the various exchange pseudopotentials in accounting for the exchange interaction, we utilize the following criteria:

1. Moments of the electron distribution †(Table II)
2. Total energy of the atom (Table III)
3. Total radial electronic distribution,
4. One-electron eigenenergies (Table IV)
4. Electron binding energies (Table V)

In all five cases the values are compared with the Hartree-Fock values²³ which take into account the exchange interaction exactly. One light alkali atom, sodium ($Z = 11$) and one heavy, closed-shell atom, mercury ($Z = 80$) were chosen to carry out these investigations.

† These are calculated from the following formulae:

$$\langle \lambda \rangle = \int_0^{\infty} |R_{n\ell}|^2 \lambda \, d\lambda$$

$$\langle \lambda^2 \rangle = \int_0^{\infty} |R_{n\ell}|^2 \lambda^2 \, d\lambda$$

$$\langle 1/\lambda \rangle = \int_0^{\infty} \frac{|R_{n\ell}|^2}{\lambda} \, d\lambda$$

23. J. B. Mann, 'Atomic Structure Calculations, Hartree-Fock Results for Hydrogen', U.S. Atomic Energy Commission, Contract No. W-7405-ENG. 36, Springfield, Va. (U.S.A.)

TABLE IIa

Moments of the Electron Distribution for Na

	HF	HFS	HS	PRESENT
$\langle r \rangle$	1S 0.1429	0.1422	0.1430	0.1429
	2S 0.7970	0.7665	0.7936	0.7951
	2P 0.7985	0.7640	0.7968	0.7947†
	3S 4.2088	4.0343	4.2372	4.219
$\langle r^2 \rangle$	1S 0.0274	0.0272	0.0275	0.0274
	2S 0.7315	0.7088	0.7632	0.7650*†
	2P 0.8221	0.7543	0.8248	0.8183
	3S 20.7050	19.1515	21.3006	20.8745
$\langle 1/r \rangle$	1S 10.607	10.6636	10.5950	10.6080
	2S 1.867	1.9069	1.8507	1.8462†
	2P 1.6966	1.7730	1.7125	1.7118
	3S 0.3014	0.3232	0.3128	0.2981

* Worse than HFS

† Worse than HS

Rest are better

TABLE IIb

Moments of the electron distribution for Hg

	HF	HFS	HS	PRESENT
$\langle r \rangle$	1S	0.01892	0.01890	0.01892
	2S	0.07961	0.07947	0.07970
	2P	0.06734	0.06709	0.06726
	3S	0.2004	0.2000	0.2010
	3P	0.1911	0.1903	0.1913
	3D	0.1670	0.1659	0.1668
	4S	0.4393	0.4383	0.4420
	4P	0.4433	0.4412	0.4455
	4D	0.4503	0.4464	0.4520
	4F	0.4692	0.4614	0.4701
	5S	1.0102	0.9869	1.0010
	5P	1.0954	1.0645	1.0860
	5D	1.4327	1.3862	1.4634
$\langle r^2 \rangle$	6S	3.3284	3.0455	3.1398
	1S	0.00048	0.00048	0.00048
	2S	0.00743	0.00740	0.00744
	2P	0.00549	0.00545	0.00547
	3S	0.0457	0.0456	0.0460
	3P	0.04221	0.0418	0.0423
	3D	0.0325	0.0321	0.0324
	4S	0.2171	0.2162	0.200
	4P	0.2228	0.2207	0.2523
	4D	0.2336	0.2297	0.2357
	4F	0.2633	0.2547	0.2651
	5S	1.1428	1.0918	1.1258
	5P	1.3551	1.2808	1.3349
	5D	2.4098	2.2557	2.5399
	6S	12.7993	10.7753	11.3898

+ Worse than HS

Rest are better

TABLE IIb cont.

	HF	HFS	HS	PRESENT
1S	79.4479	79.5130	79.4503	79.4523 [†]
2S	18.7319	18.7559	18.7081	18.7345
2P	18.7385	18.8030	18.7594	18.7389
3S	7.2840	7.2889	7.2544*	7.2650*
3P	7.2258	7.2502	7.2143	7.2267
3D	7.1436	7.1893	7.1540	7.1703 [†]
4S	3.1931	3.2039	3.1782	3.1798
4P	3.1027	3.1207	3.0928	3.0948
4D	2.9196	2.9467	2.9147	2.9181
4F	2.5835	2.6271	2.5864	2.5966 [†]
5S	1.3326	1.3488	1.3317	1.3325
5P	1.1929	1.2395	1.2186	1.2190 [†]
5D	0.9103	0.9476	0.9046	0.9092
6S	0.3761	0.4186	0.4031	0.4063 [†]

 $\langle 1/r \rangle$

* Worse than HFS

+ Worse than HS

Rest are better

FIG. 1

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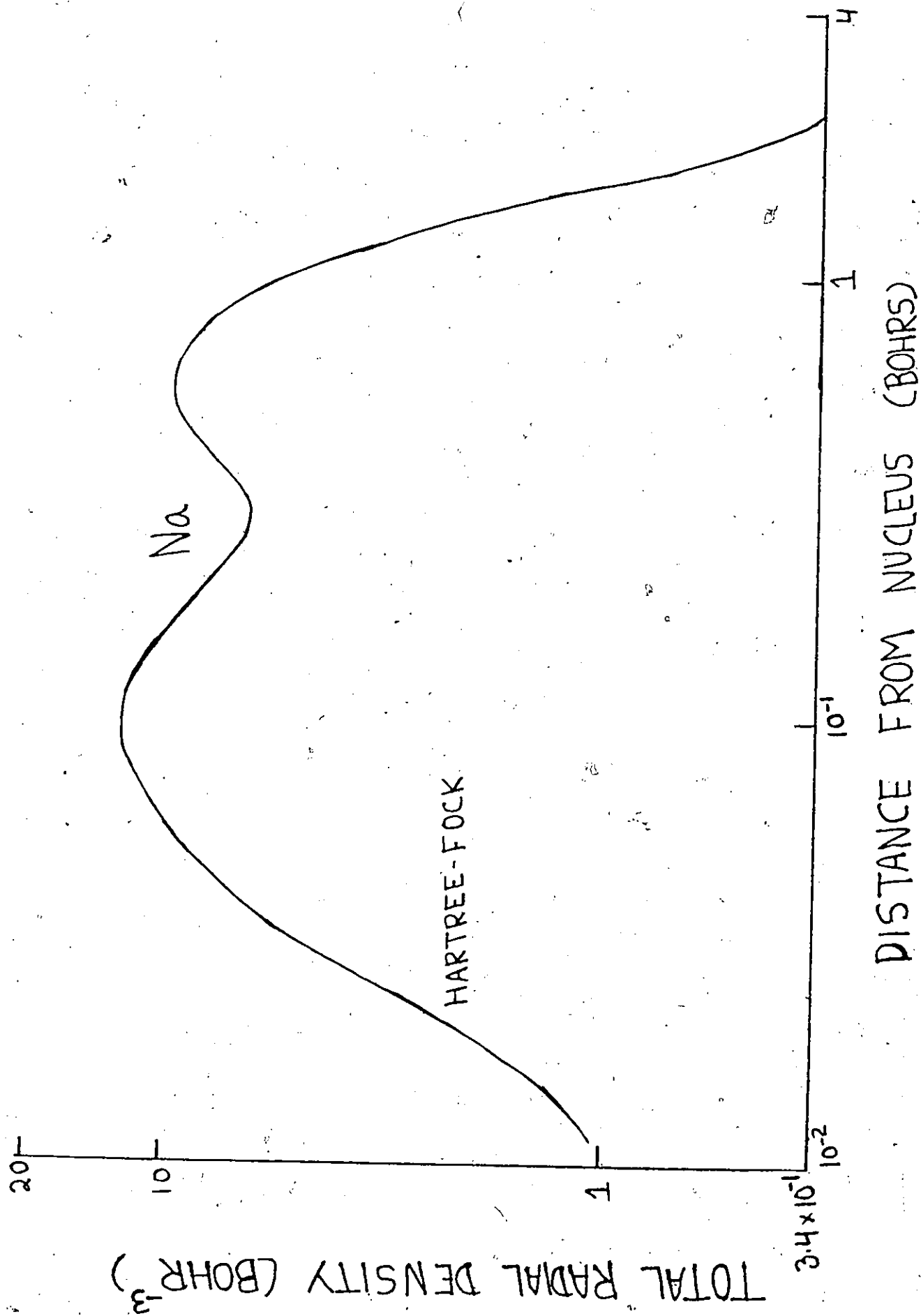


Fig. 2TOTAL RADIAL DENSITY (BOHR⁻³)

PERCENTAGE ERROR IN RADIAL DENSITY

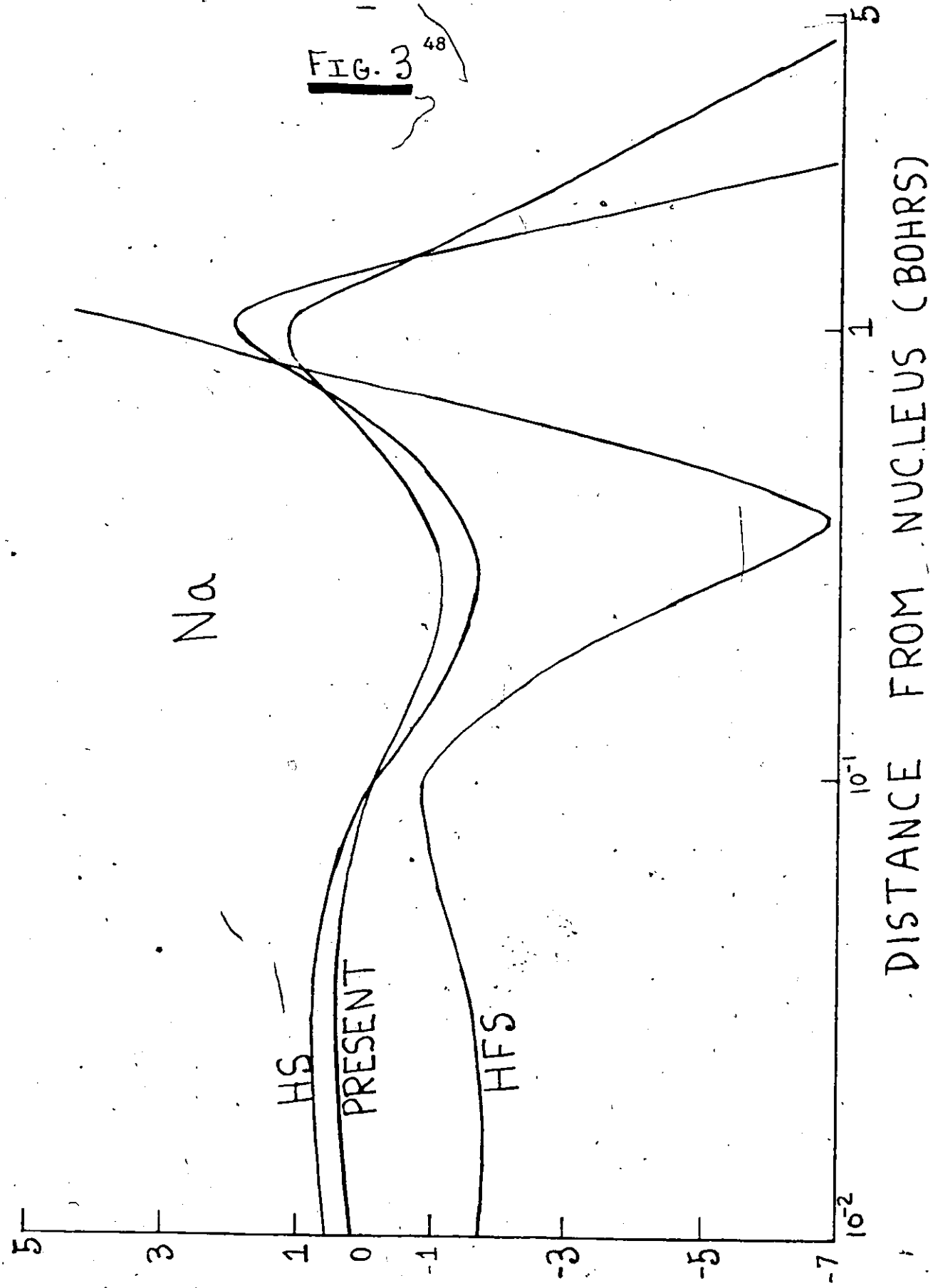


FIG. 3

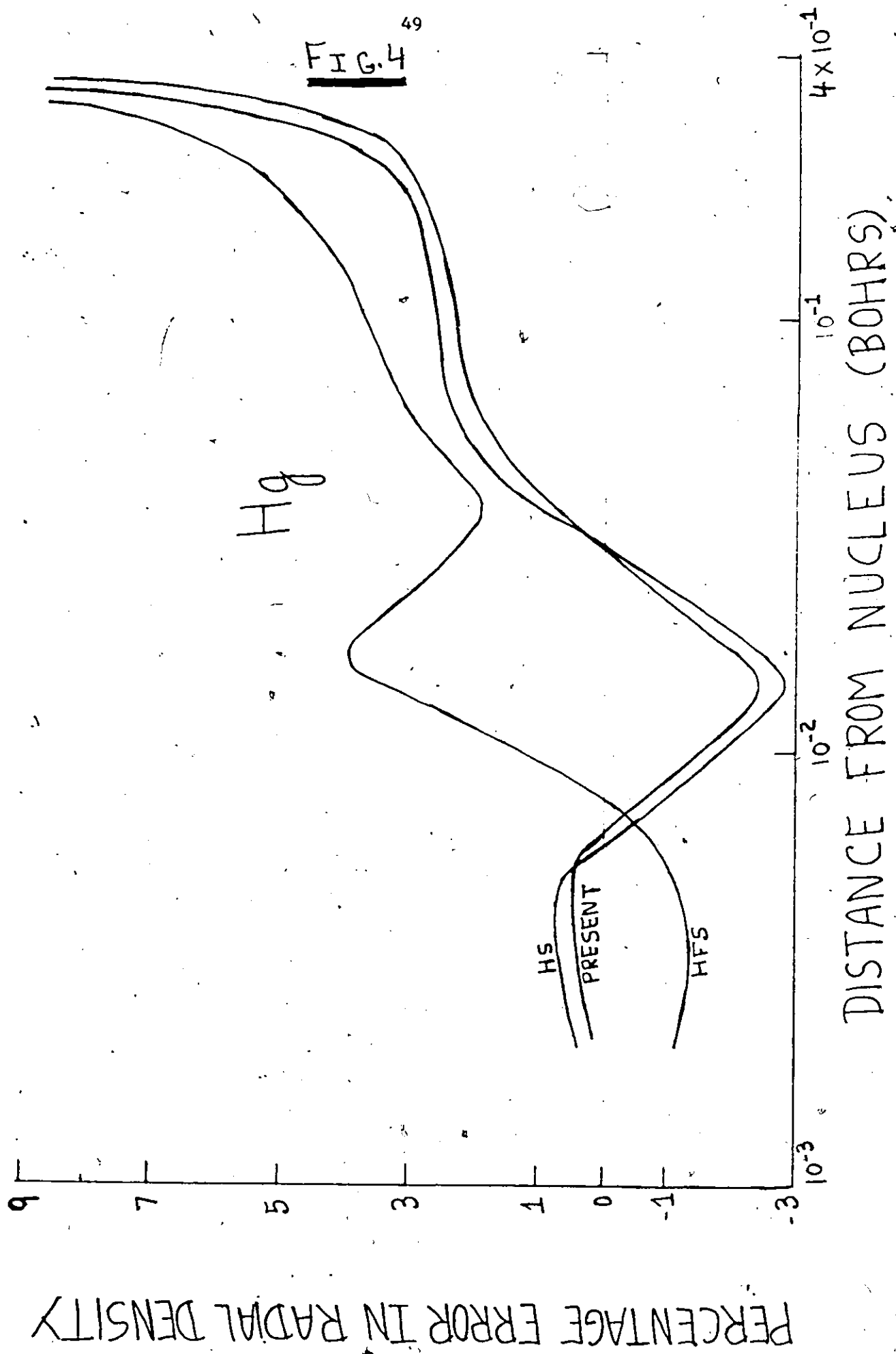


FIG. 4

TABLE III

Total Energy (Hartrees)

	HF	HFS	HS	PRESENT
Na	161.86	160.56	161.08	161.31
Hg	18409	18395	18396	18401

TABLE IV_a

One-Electron Eigenergies for Na in Hartree Units

	HF	HFS ^a	HS	PRESENT
1S	40.478	39.038	40.353	40.462
2S	2.797	2.362	2.431	2.442
2P	1.518	1.335	1.461	1.486
3S	0.1821	0.1889	0.1636	0.1812

^a The HFS results for Na and Hg (Latter's correction is used) are better without the Kohn and Sham factor of 2/3. The better results are given here.

TABLE IVb

One-Electron Eigenenergies for Hg in Hartree Units

	HF	HFS ^a	HS	PRESENT
1S	2778.639	2768.024	2776.150	2779.356
2S	470.734	465.523	465.641	467.845
2P	452.176	448.489	449.552	452.077
3S	113.136	110.256	110.192*	110.897
3P	104.341	102.072	102.044*	102.797
3D	88.145	86.674	87.027	87.931
4S	25.573	23.970	23.906*	24.109
4P	21.699	20.378	20.318*	20.516
4D	14.610	13.718	13.714*	13.910
4F	5.012	4.696	4.842	5.043
5S	4.182	3.688	3.710	3.791
5P	2.851	2.508	2.526	2.600
5D	0.714	0.637	0.649	0.699
6S	0.261	0.283	0.284*	0.297*†

^a The HFS results for Na and Hg (Latter's correction is used) are better without the Kohn and Sham factor of 2/3. The better results are given here.

* Worse than HFS

† Worse than HS

TABLE Va

Electron Binding Energies for Na

	HF	HFS	HS	PRESENT
1S	-40.47845	-39.97726	-40.43468	-40.44298
2S	-2.79702	-2.63373	-2.79226	-2.79372
2P	-1.51814	-1.34599	-1.51841	-1.51760 [†]
3S	-0.18210	-0.17598	-0.182493	-0.18681 [†]

TABLE Vb

Electron Binding Energies for Hg

	HF	HGS	HS	PRESENT
1S	2778.639	2775.856	2777.864	2778.481
2S	470.734	468.446	470.201	470.635
2P	452.176	449.801	451.608	452.073
3S	113.136	111.507	112.879	113.122
3P	104.341	102.502	103.906	104.162
3D	88.145	85.722	87.195	87.481
4S	25.573	24.648	25.509	25.606
4P	21.699	20.511	21.373	21.473
4D	14.610	13.262	14.126	14.227
4F	5.012	3.506	4.364	4.462
5S	4.182	3.814	4.211	4.189
5P	2.851	2.472	2.813	2.834
5D	0.714	0.568	0.617	0.633
6S	0.261	0.205	0.259	0.264 [†]

TABLE Vc

Percentage Error in Binding Energies

Errors are calculated with respect to the H-F approximations

Na

	HFS	HS	PRESENT
1S	1.24	0.11	.09
2S	5.84	0.17	.12
2P	11.4	0.02	.03
3S	3.36	0.22	.30

Hg

	HFS	HS	PRESENT
1S	0.10	0.03	0.006
2S	0.49	0.11	0.02
2P	0.53	0.13	0.03
3S	1.44	0.23	0.01
3P	1.76	0.42	0.17
3D	2.75	1.08	0.75
4S	3.62	.25	0.13
4P	5.47	1.49	1.04
4D	9.22	3.31	2.62
4F	30.05	12.93	10.97
5S	8.79	0.18	0.61
5P	13.28	.68	.60
5D	40.88	13.4	11.37
6S	21.14	.766	1.15

V. SUMMARY AND CONCLUSIONS

The results given in the previous chapter clearly indicate that, in a variety of tests, the present exchange approximation is fairly consistently and significantly better than the HFS and the HS approximation in approximating the Hartree-Fock results.

The present investigation was aimed at studying and accounting for the exchange effect arising out of the antisymmetry postulate. A pseudopotential was constructed in order to approximate the Hartree-Fock expression which is tedious and time consuming to calculate. The motivation was that the present pseudopotential should yield more accurate results than the ones given by other exchange approximations, namely the HFS and the HS, and should not at the same time be any more difficult to calculate. The basic idea is to incorporate into the pseudopotential, the fact that the exchange effect is non-local and that the pseudopotential should therefore contain a correlation factor which would suitably modify the electronic charge density at some point r by taking into account the exchange interaction with the charge density at r' . In other words this factor would determine the 'shape' of the so-called 'exchange hole'.

The technique used was to divide the exchange term into two parts, the SI and the IE, and treat them separately. This approach is advantageous since the SI can be treated exactly, using the Hartree approximation, thus leaving only the IE to be accounted for. The IE part is then treated by deriving a non-local interelectronic pseudopotential, based on the free electron gas model, using the kind of antisymmetry

correlation factor mentioned above. Since the total effective potential is different for each orbital the wave functions are automatically non-orthogonal. We have therefore explicitly orthonormalized them.

Even though the present pseudopotential method approximates the H-F exchange term quite closely and therefore accounts for total exchange to high precision, it solves only part of the problem of constructing an atomic potential which would yield good binding energies and wave functions. Apart from exchange, one must account for the radial and angular correlation between the electrons and also for the relativistic effects which become progressively more important as Z increases. The single-configuration Hartree-Fock approximation neglects these effects and therefore the H-F binding energies are not in close agreement with experimental ones especially for heavy atoms where these two effects become significant. Correlation effects can be taken into account by considering a linear combination of a large number of H-F configurations (represented by Slater determinants). However this again is a very tedious and time-consuming process and necessitates a pseudopotential approach.

Attempts are under way for treating these two effects. Slater has recently discussed the idea of constructing a Correlation-Exchange pseudopotential¹ and Miller² has derived a local exchange potential for the relativistic Hartree-Fock equation. A proper extension of the present work would therefore be to treat these two together i.e. to attempt to construct a Correlation-Exchange pseudopotential for the relativistic Hartree-Fock equations.

1. J. C. Slater, *Advances in Quantum Chem.*, **6**, 1 (1972).

2. L. D. Miller, *Phys. Rev.*, **7A**, 1433 (1973).

APPENDIX A

Koopman's Theorem

If we multiply the H-F equations for the i^{th} orbital

$$-\frac{\nabla_i^2}{2} \phi_i(u) - \frac{Z}{\lambda_i} \phi_i(u) + \left[\sum_j \int \phi_j^*(2) \frac{1}{\lambda_{12}} \phi_j(2) dv_2 \right] \phi_i(u) - \sum_j \delta m_{1j} m_{1j} \left[\int \phi_j^*(2) \frac{1}{\lambda_{12}} \phi_j(2) dv_2 \right] \phi_i(u) = \epsilon_i \phi_i(u) \quad (1)$$

by $\phi_i^*(u)$ and integrate over dv_1 we find that we obtain exactly the terms containing the i^{th} orbital in the expectation value of the total hamiltonian H for the atom given by:

$$\langle H \rangle = \sum_i \int \phi_i^*(u) f_i \phi_i(u) dv_u + \sum_{i,j} \int \phi_i^*(u) \phi_j^*(2) g_{12} \times [\phi_i(u) \phi_j(2) - \delta m_{1j} m_{1j} \phi_i(2) \phi_j(u)] dv_u dv_2 \quad (2)$$

This implies that if we were to remove the i^{th} orbital from the atom, leaving other orbitals unchanged, it would require energy equal to ϵ_i . Therefore, in the H-F configuration ϵ_i represents the binding energy of the electrons in the i^{th} orbital. This is the Koopman's Theorem. Explicitly we can write

$$\begin{aligned} \epsilon_i &= \langle i | H_i^0 | i \rangle + \sum_{j=1}^{i-1} \langle ij | \frac{1 - P_{ij}}{\lambda_{ij}} | ij \rangle \\ &= \langle H \rangle - \left[\sum_{j=1}^{i-1} \langle ij | H_j^0 | ij \rangle + \sum_{k < j} \langle jk | \frac{1 - P_{jk}}{\lambda_{jk}} | jk \rangle \right] \quad (3) \end{aligned}$$

where $H_i^0 = -\frac{\nabla_i^2}{2} - \frac{Z}{\lambda_i}$

and P_{ij} is the total exchange operator (both the spatial and the spin parts exchanged), given by:

$$P_{ij} = \frac{1}{2} (1 + \sigma_i \cdot \sigma_j) \exp(i \underline{k}_{ij} \cdot \underline{r}_{ij}) = P_{ji}$$

and

$\underline{\sigma}$ are the Pauli spin matrices.

From (3) it is clear that E_i is the same as the ϵ_i in (1) i.e. the ionization energy for the i^{th} orbital.

APPENDIX B

Calculation of Simple Bessel Function Integrals

We have the function:

$$h(x) = \left[3 \left(\frac{\sin x - x \cos x}{x^3} \right) \right]^2 \quad (1)$$

where $x = R\sqrt{1-\lambda}$. We write this as

$$h(x) = \frac{9}{x^2} [j_1(x)]^2 \quad (2)$$

where j_l is the spherical Bessel function of order l and

$$j_1(x) = \frac{d}{dx} j_0(x) = \frac{\sin x}{x} \quad (3)$$

We can now evaluate $\int_0^\infty dx x^n h(x)$. For $n = 1, 2$ we have the following:

$$\begin{aligned} \int_0^\infty dx x^2 h(x) &= 9 \int_0^\infty dx [j_1(x)]^2 \\ &= 9 \int_0^\infty dx \left[\frac{\cos^2 x}{x} - \frac{2 \sin x \cos x}{x^3} + \frac{\sin^2 x}{x^4} \right] \quad (4) \\ &= 1/4 \pi \end{aligned}$$

$$\begin{aligned} \int_0^\infty dx x h(x) &= 9 \int_0^\infty \frac{dx [j_1(x)]^2}{x} \quad (5) \\ &= 9 \int_0^\infty \frac{dx}{x} \left[\frac{\cos x}{x} - \frac{\sin x}{x^2} \right]^2 dx \\ &= 9/4 \end{aligned}$$

APPENDIX C

The Transformed Schroedinger Equation in Log Grid

We have the radial Schroedinger equation:

$$R_{n\ell}'' = \left[2(V-E) + \frac{\ell(\ell+1)}{\lambda^2} \right] \lambda^2 R_{n\ell} \quad (1)$$

Let $P_{n\ell} = \frac{R_{n\ell}}{\sqrt{\lambda}}$ and $\lambda = e^y$

Then $\frac{d^2 P_{n\ell}}{dy^2} = \frac{d}{dy} \left(\frac{d\lambda}{dy} \right) \frac{d}{d\lambda} \left[\frac{R_{n\ell}}{\sqrt{\lambda}} \right]$

Since

$$\begin{aligned} P_{n\ell}'' &= \frac{d}{dy} \left(\frac{d\lambda}{dy} \right) \lambda^{-1} \left[\sqrt{\lambda} R_{n\ell}' - R_{n\ell} / 2\sqrt{\lambda} \right] \\ &= (d\lambda/dy) \frac{d}{d\lambda} \left[\sqrt{\lambda} R_{n\ell}' - R_{n\ell} / 2\sqrt{\lambda} \right] \end{aligned} \quad (2)$$

Simplifying (2) we obtain:

$$P_{n\ell}'' = \lambda \sqrt{\lambda} \left[\left\{ 2(V-E) + \frac{\ell(\ell+1)}{\lambda^2} \right\} R_{n\ell} \right] + \frac{R_{n\ell}}{4\sqrt{\lambda}} \quad (3)$$

which upon substitution for $R_{n\ell}$, in terms of $P_{n\ell}$, leads to:

$$\begin{aligned} P_{n\ell}'' &= \left[2\lambda^2 (V-E) + \left(\ell + \frac{1}{2} \right)^2 \right] P_{n\ell} \\ &= E_q [100] \end{aligned} \quad (4)$$

APPENDIX D

Calculation of Binding Energy

We can rewrite Eq. (114) in three separate parts

$$E_i = - \left\langle i \left| -\frac{\nabla_i^2}{2} - \frac{Z}{\lambda_i} \right| i \right\rangle + \sum_j \left\langle ij \left| \frac{1}{\lambda_{12}} \right| ij \right\rangle - \sum_j \left\langle ij \left| \frac{1}{\lambda_{12}} \right| ji \right\rangle \quad (1)$$

where $\frac{1}{\lambda_{12}} = \sum_{l=0}^{\infty} \left[\frac{\lambda_1^{l+1}}{\lambda_2^{l+1}} \right] \left[\frac{4\pi}{2l+1} \right] \sum_m Y_{lm}(\hat{\lambda}_1) Y_{lm}(\hat{\lambda}_2)$

The first term on RHS is simply given by the equation

$$\left(-\frac{\nabla_i^2}{2} + V_i + E_i \right) |i\rangle = 0 \quad (2)$$

therefore

$$\left\langle i \left| -\frac{\nabla_i^2}{2} - \frac{Z}{\lambda_i} \right| i \right\rangle = \left\langle i \left| E_i - V_i - \frac{Z}{\lambda_i} \right| i \right\rangle \quad (3)$$

' E_i ' is the ONE ELECTRON EIGENVALUE

The second and the third terms on RHS represent the direct electrostatic (DEI) and the exchange (EXI) interactions respectively. We first consider DEI,

$$DEI = \sum_{m_j} \left\langle ij \left| \frac{1}{\lambda_{12}} \right| ij \right\rangle \cdot 2 \quad (4)$$

where m_j is the magnetic quantum number and '2' accounts for the two electrons being present in two spin states corresponding to each m_j . Expanding

$$(4): \quad DEI = 2 \int d\lambda_1 \int d\lambda_2 \left[\int d\hat{\lambda}_1 \int d\hat{\lambda}_2 \sum_{m_j} Y_{l_j m_j}^{l_j}(\hat{\lambda}_1) Y_{m_j}^{l_j}(\hat{\lambda}_2) \times \right. \\ \left. Y_{l_j m_j}^{l_j}(\hat{\lambda}_1) Y_{m_j}^{l_j}(\hat{\lambda}_2) \right] \left[\frac{1}{\lambda_{12}} |R_1(1)|^2 |R_2(2)|^2 \right] \quad (5)$$

using the addition theorem:

$$\sum_m Y_l^m(\hat{x}_1) Y_l^m(\hat{x}_2) = \frac{2l+1}{4\pi} P_l(\hat{x}_1 \cdot \hat{x}_2)$$

we have

$$DEI = \sum_j \left[2 \int d\lambda_1 \int d\lambda_2 \frac{1}{\lambda_{12}} |R_i(1)|^2 |R_j(2)|^2 \frac{2l_j+1}{4\pi} \times Y_{l_i, m_i}^{l_i}(\hat{x}_1) Y_{l_j, m_j}^{l_j}(\hat{x}_2) \right] \quad (6)$$

which in the average over m results in ($i=0$):

$$DEI = \sum_j \int_0^\infty d\lambda_1 \int_0^\infty d\lambda_2 \frac{1}{\lambda_{12}} |R_i(1)|^2 |R_j(2)|^2 \omega_j \quad (7)$$

where $\omega_j = 2(2l_j+1)$. We then compute DEI from:

$$DEI = \sum_j \left[\int_0^\infty |R_i(\omega)|^2 d\lambda_1 \left\{ \frac{1}{\lambda_1} \int_0^\infty \omega_j |R_j(2)|^2 d\lambda_2 + \int_0^\infty \frac{\omega_j |R_j(\omega)|^2 d\lambda_2}{\lambda_2} \right\} \right] \quad (8)$$

Next we consider the exchange integral

$$EXI = \sum_{m_j} \langle i j | \frac{1}{\lambda_{12}} | j i \rangle \quad (9)$$

Unlike DEI the factor '2' is absent here since we only consider half the electrons which have the same spin as the i^{th} electron. We then write (9)

in integral form as:

$$EXI = \sum_{m_j} \left\{ \sum_l \frac{4\pi}{2l+1} \left[\int_0^\infty d\lambda_1 \int_{\lambda_1}^\infty \frac{\lambda_1^l}{\lambda_2^{l+1}} d\lambda_2 + \int_0^\infty d\lambda_1 \int_0^{\lambda_1} \frac{\lambda_2^l}{\lambda_1^{l+1}} d\lambda_2 \right] \times R_i(1) R_i(2) R_j(1) R_j(2) \left[\int d\hat{x}_1 \int d\hat{x}_2 Y_{l_i, m_i}^{l_i}(\hat{x}_1) Y_{l_j, m_j}^{l_j}(\hat{x}_2) Y_{l_i, m_i}^{l_i}(\hat{x}_1) Y_{l_j, m_j}^{l_j}(\hat{x}_2) \right] \right\} \quad (10)$$

We know that for a function $f(\lambda_1, \lambda_2)$, uniformly convergent in

region λ_1 and λ_2 we have:

$$\int_0^\infty d\lambda_1 \int_{\lambda_1}^\infty d\lambda_2 f(\lambda_1, \lambda_2) = \int_0^\infty d\lambda_2 \int_0^{\lambda_2} d\lambda_1 f(\lambda_1, \lambda_2) = \int_0^\infty d\lambda_1 \int_0^\infty d\lambda_2 f(\lambda_1, \lambda_2)$$

Hence Eq. (10) becomes:

$$EXI = \sum_{m_j} \left\{ \sum_{l,m} \frac{4\pi}{2l+1} \left[2 \int_0^\infty d\lambda_1 \int_0^{\lambda_1} d\lambda_2 \frac{\lambda_2^l}{\lambda_1^{l+1}} R_i(\lambda_1) \bar{R}_j(\lambda_2) R_j(\lambda_1) R_i(\lambda_2) \right] \times \right. \\ \left. \left[Y_{l,m_j}^{l_j}(\hat{1}) Y_{l,m_j}^{l_j}(\hat{2}) Y_{l,m_i}^{l_i}(\hat{1}) Y_{l,m_i}^{l_i}(\hat{2}) Y_{l,m}^{l_i}(\hat{1}) Y_{l,m}^{l_i}(\hat{2}) \right]^{(11)} \right\} \quad (11)$$

where the Clebsch-Gordon coefficients are calculated from Appendix E. For computational purposes we rewrite Eq. (12) as:

$$EXI = \sum_i \left[2 \int_0^\infty d\lambda_1 \frac{R_i(\lambda_1) R_j(\lambda_1)}{\lambda_1^{l+1}} \int_0^{\lambda_1} d\lambda_2 R_j(\lambda_2) R_i(\lambda_2) \lambda_2^l d\lambda_2 \right. \\ \left. \times |<l_i, 0 | l_j, 0; l, 0>|^2 \right] \quad (13)$$

For a given 'i' Eq. (13) is summed over all 'j's. Combining Eqs. (3), (8) and (13) we obtain Eq. (114) for the binding energy of the i^{th} orbital.

APPENDIX E

Clebsch-Gordon Coefficients[†]

We know that for Spherical Harmonics we can define:

$$C_a^k = \left[\frac{4\pi}{2k+1} \right]^{\frac{1}{2}} Y_{ka}(\theta, \phi) \quad (1)$$

and that

$$\begin{aligned} \langle LM | C_a^k | L'M' \rangle &= (-1)^{2k} \langle LM | L'M', ka \rangle \langle L || C^k || L' \rangle \\ &= (-1)^{2k+ka} \langle LM | L'M', ka \rangle \langle L' 0 | L 0, k 0 \rangle \quad (2) \end{aligned}$$

From (1)

$$\langle LM | Y_a^k | L'M' \rangle = \left[\frac{2k+1}{4\pi} \right]^{\frac{1}{2}} \langle LM | C_a^k | L'M' \rangle \quad (3)$$

Hence

$$\begin{aligned} &\sum_{M'a} \langle LM | Y_a^k | L'M' \rangle \langle L'M' | Y^{ka} | LM \rangle \\ &= (-1)^k \langle L' 0 | L 0, k 0 \rangle \langle L 0, k 0 | L' 0 \rangle \sum_{M'a} \langle LM | L'M', ka \rangle \langle L'M', ka | LM \rangle \\ &= (-1)^k \left[\frac{2k+1}{4\pi} \right] |\langle L' 0 | L 0, k 0 \rangle|^2 \quad (4) \times \left[\frac{2k+1}{4\pi} \right] \end{aligned}$$

we are interested in evaluating a factor of the form $|\langle l_3 0 | l_1 0 ; l_2 0 \rangle|^2$

(see Eq. (3)). For a few special cases we have, from (4),

$$|\langle l_3 0 | l_3 0 ; 0 0 \rangle|^2 = \frac{1}{2l_3+1}$$

$$|\langle l_3 0 | l_3 0 ; l_2^{\text{ODD}} 0 \rangle|^2 = 0$$

$$|\langle l_3 0 | l_3 0 ; l_2^{\text{EVEN}} 0 \rangle|^2 = \frac{(2l_3 - l_2)! l_2! (l_3 + \frac{l_2}{2})!}{(2l_3 + l_2 + 1)! (\frac{l_2}{2}!)^2 (l_3 - \frac{l_2}{2})!}$$

[†] A. R. Edmonds, 'Angular Momentum in Quantum Mechanics' Princeton Univ. Press, Princeton, (1957).

In general:

$$| \langle l_3 0 | l_1 0 ; l_2 0 \rangle |^2 = 2^{l_3+1} \frac{(2\lambda_3)!(2\lambda_2)!(2\lambda_1)!}{(2\lambda_1+2\lambda_2+2\lambda_3+1)!} \left[\frac{(\lambda_1+\lambda_2+\lambda_3)!}{\lambda_1! \lambda_2! \lambda_3!} \right]^2 \quad (5)$$

FOR $(l_1+l_2+l_3)$ EVEN

and

$$= 0 \quad \text{FOR } (l_1+l_2+l_3) \text{ ODD}$$

In Eq. (5) we have used

$$\lambda_1 = \frac{1}{2} [l_2 + l_3 - l_1]$$

$$\lambda_2 = \frac{1}{2} [l_3 + l_1 - l_2]$$

$$\lambda_3 = \frac{1}{2} [l_1 + l_2 - l_3]$$

APPENDIX F

Spherical Bessel functions satisfy the following equations:

$$(\nabla^2 + k^2) j_\ell(kr) Y_\ell^m(\hat{r}) = 0 \quad (1)$$

$$\left[\frac{1}{r} \frac{d^2}{dr^2} + k^2 - \frac{\ell(\ell+1)}{r^2} \right] j_\ell(kr) = 0 \quad (2)$$

we note that

$$\int_0^\infty dr r j_{\ell'}(kr) \frac{d^2}{dr^2} [r j_\ell(kr)] = \int_0^\infty dr r j_\ell(kr) \frac{d^2}{dr^2} [r j_{\ell'}(kr)] \quad (3)$$

It follows then, from (2), that

$$\int_0^\infty dr r^2 j_{\ell'}(kr) j_\ell(kr) \left[(k^2 - k'^2) - \frac{\ell(\ell+1) - \ell'(\ell'+1)}{r^2} \right] = 0 \quad (4)$$

$$\therefore \int_0^\infty dr j_\ell(kr) j_{\ell'}(kr) = \frac{k'^2 - k^2}{[\ell(\ell+1) - \ell'(\ell'+1)]} \int_0^\infty dr r^2 j_\ell(kr) j_{\ell'}(kr) \quad (5)$$

For $\ell = \ell'$ Eq. (5) is simply the orthogonality condition. Consider $\ell = 0, \ell' = 1$:

$$\int_0^\infty dr j_0(kr) j_1(k'r) = \left[\frac{k'^2 - k^2}{2} \right] \int_0^\infty dr r^2 j_0(kr) j_1(k'r) \quad (6)$$

Since $j_0(x) = \frac{\sin x}{x}$ and $j_1(x) = \frac{\sin x - x \cos x}{x^2}$

$$\begin{aligned} I &\equiv \int_0^\infty dr j_0(kr) j_1(k'r) = \left(\frac{k'^2 - k^2}{2} \right) \int_0^\infty dr r^2 j_0(kr) j_1(k'r) \\ &= \frac{k'^2 - k^2}{2kk'^2} \int_0^\infty dr \left[\frac{\sin kr \sin k'r}{r} - k' \sin kr \cos k'r \right] \\ &= \frac{k'^2 - k^2}{4kk'^2} \ln \left| \frac{k' + k}{k' - k} \right| + \frac{1}{2k'} \quad (7) \end{aligned}$$

AVERAGING OVER k :

$$\langle I \rangle = \frac{3}{k_F^3} \int_0^{k_F} dk k^2 I = \frac{3}{4k_F^5} \int_0^{k_F} (k_F^2 - k^2) \left[\ln(k_F^2 - k^2) - 2 \ln(k_F - k) \right] + \frac{1}{2k_F} \quad (8)$$

let $x = k_F^2 - k^2$ and $y = k_F - k$, then:

$$\begin{aligned} \langle I \rangle &= \frac{3}{5k_F^5} \int_0^{k_F} dx x \ln x - \frac{3}{2k_F^5} \int_0^{k_F} dy (k_F - y)(2k_F - y)y \ln y + \frac{1}{2k_F} \\ &= \frac{1}{4k_F} + \frac{1}{2k_F} = \frac{3}{4k_F} \quad (9) \end{aligned}$$

PART 2

ABSTRACT

A semi-empirical parametrized model potential is constructed using a one parameter perturbative variation-iteration method. The following report discusses the theory and the computational methods for the computer program. Preliminary results indicate that the program is capable of constructing a potential which would yield eigenenergies within the experimental accuracy of the empirical data. The eigenfunction of the potential should also, therefore, be very accurate.

I. INTRODUCTION

Model potential techniques are in considerable use in solid state theory¹ and atomic and molecular physics^{2,3} for the calculation of the properties of solids, atoms and molecules. In scattering theory⁴ we use this technique to construct the scattering potential from scattering data.

Recently several authors have devised methods for constructing atomic potentials from spectroscopic data (Bottcher 1971, Bardsley 1971, Norcross 1972)⁵. The basic idea is to determine a functional form for the potential which would fit the experimental data given in terms of the term values for the ground state and excited levels. Alkali atoms are most suited to this approach since such data is readily available and because many properties of alkali atoms depend mainly on the behaviour of the valence electron.

The main idea is to start with some parametrized form for the potential, $V(\underline{\alpha}, \lambda)$ where $\underline{\alpha} = (\alpha_1, \dots, \alpha_n)$ are the 'n' parameter, and to vary these parameters until the potential reproduces the input experimental results to some accuracy. Two of the authors mentioned above (Bardsley and Norcross) have devised functional forms for the potential with two adjustable parameters and have reported quite good results for several properties of alkali atoms. In the present work we shall attempt to

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1. W. A. Harrison, 'Pseudopotentials in the Theory of Metals' (Benjamin, New York, 1966).
 2. L. Szasz and McGinn, J. Chem. Phys. 42, (1965).
 3. J. Callaway and P. S. Laghos, Phys. Rev. 187, 192 (1969).
 4. Marchenko and Agranovich, 'Inverse Problem in Scattering Theory', (Academic Press, New York).
 5. C. Bottcher, J. Phys. B. Atom. Molec. Phys., 4, 1140 (1971).
J. N. Bardsley, Chem. Phys. Letters, 7, No. 5, (1970).
D. W. Norcross, Phys. Rev. A, 7, 2 (1973).

construct a model potential which will fit several more parameters and which should therefore yield more accurate results. We shall first describe some of the methods, and the theory behind them, used to solve this problem and then we shall discuss the algorithm developed in the present work.

1. Basic Methods

Given the radial Schroedinger equation

$$\left[\frac{d^2}{d\lambda^2} - \frac{l(l+1)}{\lambda^2} + 2[E_i - V(\lambda)] \right] R_i(\lambda) = 0 \quad (1)$$

we know from First-Order Perturbation Theory (FOPT) that if the potential $V(\lambda)$ is changed by a small amount $\Delta V(\lambda)$, then the corresponding variation in the eigenenergy E_i is:

$$\delta E_i \cong \int_0^\infty R_i^2(\lambda) \Delta V(\lambda) d\lambda \quad (2)$$

For a potential of the form $V(\underline{\alpha}, \lambda)$, we can write the perturbation ΔV as:

$$\Delta V = \sum_{i=1}^N \left(\frac{\partial V}{\partial \alpha_i} \right) \delta \alpha_i \quad (3)$$

According to (3) and (2) we can now vary the components of the vector $(\underline{\alpha})$ to affect a change in $V(\lambda)$ such that its eigenenergies will be closer to the experimental ones. One can adopt two different approaches based on this perturbation-variation method.

The first one (used by Bottcher⁶) consists in varying all the parameters in the potential simultaneously such that the square deviation of the eigenenergies of the potential from the experimental ones is minimized. The second approach, adopted in the present work, is to consider

6. C. Bottcher, ref. 5

one eigenvalue at a time and to vary the corresponding parameter until the state at that energy converges to an eigenstate of the potential. At the same time, other eigenvalues already matched are kept stationary by varying their corresponding parameters as well.

We shall briefly outline the first approach (Bottcher's work is chosen for example) before elaborating on the present one.

2. Simultaneous Parameter Variation-Iteration Method

We begin with a trial potential of the form

$$V(\underline{\alpha}, \lambda) = V_0(\lambda) + \sum_{i=1}^N \alpha_i U_i(\lambda) \quad (4)$$

where $V_0(\lambda)$ is the initial potential and $U_i(\lambda)$ is the expansion set with α_i as the linear parameters. The choice of $V_0(\lambda)$ is restricted by the requirement that the initial potential be close to the actual one in order that FOPT may be valid. Bottcher takes $V_0(\lambda)$ to be the Hartree-Fock potential with polarization terms added, and the set $\{U_i\}$ to be

$$U_i(\lambda) = \lambda^{n_i} \exp(-\lambda/\lambda_i)$$

Assuming that we have the set of experimental eigenenergies $\{E_i^x\}$, we solve Eq. (1) with the trial $V(\lambda)$ for the set of radial wave functions $\{R_i\}$. We know from Eq. (2) that for a given perturbation ΔV in the potential the corresponding variation in the eigenenergy will be given by

$$\delta E_i = \sum_{j=1}^N \delta \alpha_j U_{ij} \quad (5)$$

where

$$V_{ij} = \int_0^{\infty} R_i^2(\lambda) V_j(\lambda) d\lambda \quad (6)$$

we then have a set of linear equations through which we can determine for any set $\{\alpha_i\}$. If we choose $\delta E_i = E_i^x - E_i$, i.e. to be the difference between the experimental eigenenergies and the eigenenergies of the potential, then we can obtain an improved set of parameters $\{\alpha_i^I\}$ by solving

$$\sum_{j=1}^N V_{ij} (\alpha_j^I - \alpha_j^0) = (E_i^x - E_i) \quad (7)$$

where α_j^0 are the trial parameters.

Eqs. (7) are solved iteratively until we obtain a set of parameters which yields a potential with eigenenergies $\{E_i\}$ as close to $\{E_i^x\}$ as possible.

Bottcher notes that Eq. (7) is equivalent to a variational principle for the potential. From the Hellman-Feynman theorem⁷

$$\frac{\partial E}{\partial \lambda} = \langle \Psi | \frac{\partial H}{\partial \lambda} | \Psi \rangle \quad (8)$$

where λ is a parameter in the hamiltonian. It can be deduced that

$$\delta \langle \Psi_i | V - E_i | \Psi_i \rangle = 0 \quad (9)$$

from which Eq. (7) follows immediately. \square

7. E. Merzbacher, 'Quantum Mechanics', pg. 442, (John Wiley Inc., New York).

II. ONE-PARAMETER VARIATION-ITERATION METHOD

As mentioned above, the technique involved in this approach is to vary one parameter at a time instead of all at once. This method is expected to have the following advantages over the previous method:

1. The numerical process should be more stable since we are effectively working with only one parameter at a time.
2. We can impose strict accuracy requirements since the convergence of the process for each parameter is independent of others i.e. the accuracy of one does not have to be sacrificed in order to satisfy a convergence criterion for all. For example in Bottcher's method one settles for a least square solution of Eq. (7) by minimizing the N-dimensional function

$$\sum_{i=1}^N \left[\sum_{j=1}^N U_{ij} (\alpha_j^x - \alpha_j) - (E_i^x - E_i) \right]^2 \quad (10)$$

3. The problem is reduced from an N-dimensional one to a one-dimensional problem (to be solved N-times for N parameters).

The advantages and disadvantages of this method will be discussed further towards the end when it will be compared with other methods.

We now give an analysis of the theory and the technique involved in the present work.

1. Theory

In the previous section we noted that one way to construct the model potential is to vary the parameter until the eigenenergies match with the input spectroscopic values. This is the approach adopted by Bottcher. However, for an eigenstate the eigenenergy E is not sensitive

to first order to a perturbation in the eigenfunction but to second order i.e.

$$\Delta E = O[\Delta\psi]^2 \quad (11)$$

Therefore a slight discrepancy in the eigenenergy may lead to a considerable discrepancy in the wave function. For example, if the eigenenergy is off by 1%, then the error in the wave function might be of the order of 10%. Therefore in the present work we use the wave function itself as the test criterion; varying the parameters in the potential until the wave function has the right behaviour. We thereby simplify the computation (1) by having a more sensitive monitor of the accuracy of eigenenergies and (2) because it is not necessary to search for the eigenenergies, a step requiring several integrations of the Schroedinger equations at different trial energies, before the monitoring proceeds.

For the purpose of the present work we can divide the atomic potential into two distinct expressions, one representing the short range interactions (SR) and the other for the long range part (LR) and the asymptotic behaviour i.e. in general we can write:

$$V(\lambda) = V_{SR}(\lambda) + V_{LR}(\lambda) \quad (12)$$

The variable parameters may be placed in either or both of the two terms. Basically the form of the parameters is chosen so that the short range potential for the valence electron should represent the departure from straight Coulomb potential, $-\frac{Z}{\lambda}$, due to shielding by the core electrons. The long range potential should represent the Coulomb attraction of the core plus polarization effects and any other asymptotic behaviour. With these considerations in mind we write, in general, the effective atomic potential for an atom with atomic number Z and core charge z , as:

$$V(\alpha, \lambda) = - \left[\frac{(Z-\alpha)}{\lambda} \lambda^{n_1} e^{-\alpha_1 \lambda} (1 + \alpha_2 \lambda^{n_2} + \alpha_3 \lambda^{n_3} + \dots + \alpha_N \lambda^{n_N}) + \left\{ \frac{\frac{1}{2} A_d \lambda^2}{(\alpha_d^2 + \lambda^2)^3} + \frac{(A_q - 3\beta a_0) \lambda^2}{(\alpha_q^2 + \lambda^2)^4} + \frac{\beta}{\lambda} \right\} \right] \quad (13)$$

The two terms on RHS represent V_{SR} and V_{LR} respectively. A_d and A_q are the dipole and the quadrupole polarizabilities respectively. Along with the 'N' variable parameters in V_{SR} we can also vary α_d and α_q , the dipole and the quadrupole cut-off lengths respectively, to modify V_{LR} . Eq. (12) has the right behaviour as $\lambda \rightarrow 0$ and $\lambda \rightarrow \infty$ since

$$\begin{aligned} \lim_{\lambda \rightarrow 0} V(\alpha, \lambda) &= -Z/\lambda \\ \text{and } \lim_{\lambda \rightarrow \infty} V(\alpha, \lambda) &= -\beta/\lambda \end{aligned} \quad (14)$$

(atomic units are used throughout). It is clearly desirable to choose the potential such that it will be most responsive to the parameter representing the region around which the expectation value, $\langle \lambda \rangle$, of the corresponding eigenfunction lies. Therefore the short range part is constructed so as to ensure that successive parameters are variable coefficients in terms that influence the potential within regions that are successively farther away from the origin. In Eq. (12), therefore, we let $n_1 < n_2 < \dots < n_N$.

For example, the form could be:

$$V_{SR}(\lambda) = - \left(\frac{Z-\alpha}{\lambda} \right) \left[e^{-\alpha_1 \lambda} + \alpha_2 \lambda e^{-\alpha_1 \lambda} + \alpha_3 \lambda^2 e^{-\alpha_1 \lambda} + \alpha_4 \lambda^3 e^{-\alpha_1 \lambda} \right] \quad (15)$$

For the n^{th} term, in Eq. (14), the maximum of $V(r)$ with respect to r lies at $\lambda_{\text{max}} = \frac{n_i}{\alpha_1}$ + i.e. its value goes up with 'n', the index of r . The total number of parameters in the potential must clearly equal the number of eigenvalues required to be fitted into the potential.

* The maximum of $\lambda^n e^{-\alpha_1 \lambda}$, obtained simply from:

$$\frac{d}{d\lambda} (\lambda^n e^{-\alpha_1 \lambda}) = 0$$

In addition to the short-range and the long range parts, we also incorporate, into the potential, the fine structure of the electron due to the spin-orbit coupling⁸. This part of the potential is labelled as V_{SO} and is given by⁹:

$$V_{SO} = \frac{1}{2} \alpha^2 \frac{1}{\lambda} \frac{dV}{d\lambda} \left[1 + \frac{1}{4} \alpha^2 V(\lambda) \right]^{-2} \underline{L} \cdot \underline{S} \quad (16)$$

The term in square brackets is the relativistic correction to the spin orbit coupling¹⁰. The total effective potential is then

$$V_{eff}(\alpha, \lambda) = V_{SR} + V_{LR} + V_{SO} \quad (17)$$

2. The Algorithm

This section outlines the algorithm adopted. The details involved in each step are given in the next section.

We begin with the trial potential described above, with suitably chosen parameters, and calculate $|\Phi_1\rangle$ from Eq. (1) using this potential and the corresponding spectroscopic term values. The $|\Phi_1\rangle$ obtained will not in general have the right number of nodes since the trial potential might not be good enough. We therefore use the WKB approximation to modify in the potential such that the phase integral $\int_{\lambda_1}^{\lambda_2} k_1 d\lambda = (n_1 - l_1 - \frac{1}{2})\pi$. This procedure (details given in next section) ensures that we have a good

8. J. D. Jackson, 'Classical Electrodynamics', (John Wiley and Sons, Inc., New York).

9. D. W. Norcross, Phys. Rev. A, 7, No. 2, (1973).

10. E. V. Condon and G. H. Shortley, 'The Theory of Atomic Spectra', pg. 130-131, (Cambridge).

starting potential which yields wave functions that have the right number of nodes.

After we make sure that $|P_1\rangle$ has the right number of nodes, we test $|P_2\rangle$ to see if it behaves like the regular solution of the Schroedinger equation as $\lambda \rightarrow 0$ i.e.

$$P \sim_{\lambda \rightarrow 0} \lambda^{l+1} \quad (18)$$

We then calculate the amount $\delta\alpha_1$ needed to change α_1 such that Eq. (18) is satisfied. Having obtained $|P_1\rangle$ we proceed to $|P_2\rangle$ and the corresponding parameter α_2 . Again we calculate $\delta\alpha_2$ required to change such that $|P_2\rangle$ behaves like (18). However, if we change α_2 alone then the potential will no longer yield the first eigenfunction correctly and hence we must, at the same time, also change α_1 by some amount $\delta\alpha_1$ such that $|P_1\rangle$ remains a stationary state. According to First Order Perturbation Theory this implies that for a perturbation ΔV , induced by $\delta\alpha_1$ and $\delta\alpha_2$, we require

$$\delta E_1 = \langle P_1 | \Delta V | P_1 \rangle = 0 \quad (19)$$

where

$$\Delta V \approx \left(\frac{\partial V}{\partial \alpha_1} \right) \delta\alpha_1 + \left(\frac{\partial V}{\partial \alpha_2} \right) \delta\alpha_2 \quad (20)$$

Therefore from Eqs. (17) and (18)

$$\delta\alpha_2 = - \frac{\langle P_1 | \frac{\partial V}{\partial \alpha_2} | P_1 \rangle}{\langle P_1 | \frac{\partial V}{\partial \alpha_1} | P_1 \rangle} \delta\alpha_1 \quad (21)$$

which is the change in α_2 corresponding to $\delta\alpha_1$ such that $|P_1\rangle$ remains

stationary i.e. $\delta E_1 = 0$. In general, when we are adjusting the n^{th} parameter to fit the n^{th} eigenfunction, then in order to keep the other $(n - 1)$ eigenfunctions (already fitted) stationary, we have to solve the following set of linear simultaneous equations:

$$\begin{aligned} \langle 1 | \frac{\partial V}{\partial \alpha_1} | 1 \rangle \delta \alpha_1 + \dots + \langle 1 | \frac{\partial V}{\partial \alpha_n} | 1 \rangle \delta \alpha_n &= 0 \\ \vdots & \\ \langle n-1 | \frac{\partial V}{\partial \alpha_1} | n-1 \rangle \delta \alpha_1 + \dots + \langle n-1 | \frac{\partial V}{\partial \alpha_n} | n-1 \rangle \delta \alpha_n &= 0 \end{aligned} \quad (22)$$

Eq. (20) follows directly from (17), (18) and (19). In the more compact matrix notation we can write

$$\underline{M} \cdot \underline{\delta \alpha} = \underline{0} \quad (23)$$

where

$$\underline{\delta \alpha} = \begin{pmatrix} \delta \alpha_1 \\ \vdots \\ \delta \alpha_n \end{pmatrix}; \quad M_{ij} = \langle i | \frac{\partial V}{\partial \alpha_j} | i \rangle$$

Since we can determine $\delta \alpha_n$ from the behaviour of $|n\rangle$ near the origin, Eq. (22)

is reduced to a set of $n - 1$ simultaneous equations in $n - 1$ unknowns,

$\delta \alpha_1, \dots, \delta \alpha_{n-1}$. Solving (22), then, gives us the changes in $\alpha_1, \dots, \alpha_n$, such that $|1\rangle, \dots, |n-1\rangle$ remain unperturbed by the perturbation induced by $\delta \alpha_n$.

Thus we observe the n^{th} wave function near the origin and calculate $\delta \alpha_n$, the change in the corresponding parameter, such that Eq. (18) is satisfied. Then we calculate the corresponding changes in the remaining $(n - 1)$ parameters from First Order Perturbation Theory and obtain a new set of parameters

$$\underline{\alpha'} = \underline{\alpha} + \underline{\delta \alpha} \quad (24)$$

Putting the new parameters in the potential, we repeat the above process until we obtain the optimum set of parameters with which the potential yields the 'n' eigenfunctions correctly and its eigenenergies match with the spectroscopic ones to some given accuracy.

3. Computational Description of the Method

With respect to the radial wave function, for a given energy level 'E' and effective atomic potential $V_{eff}(\lambda)$, we can divide the entire region from $r = 0$ to $r = \infty$, in three distinct parts illustrated in the following diagram:

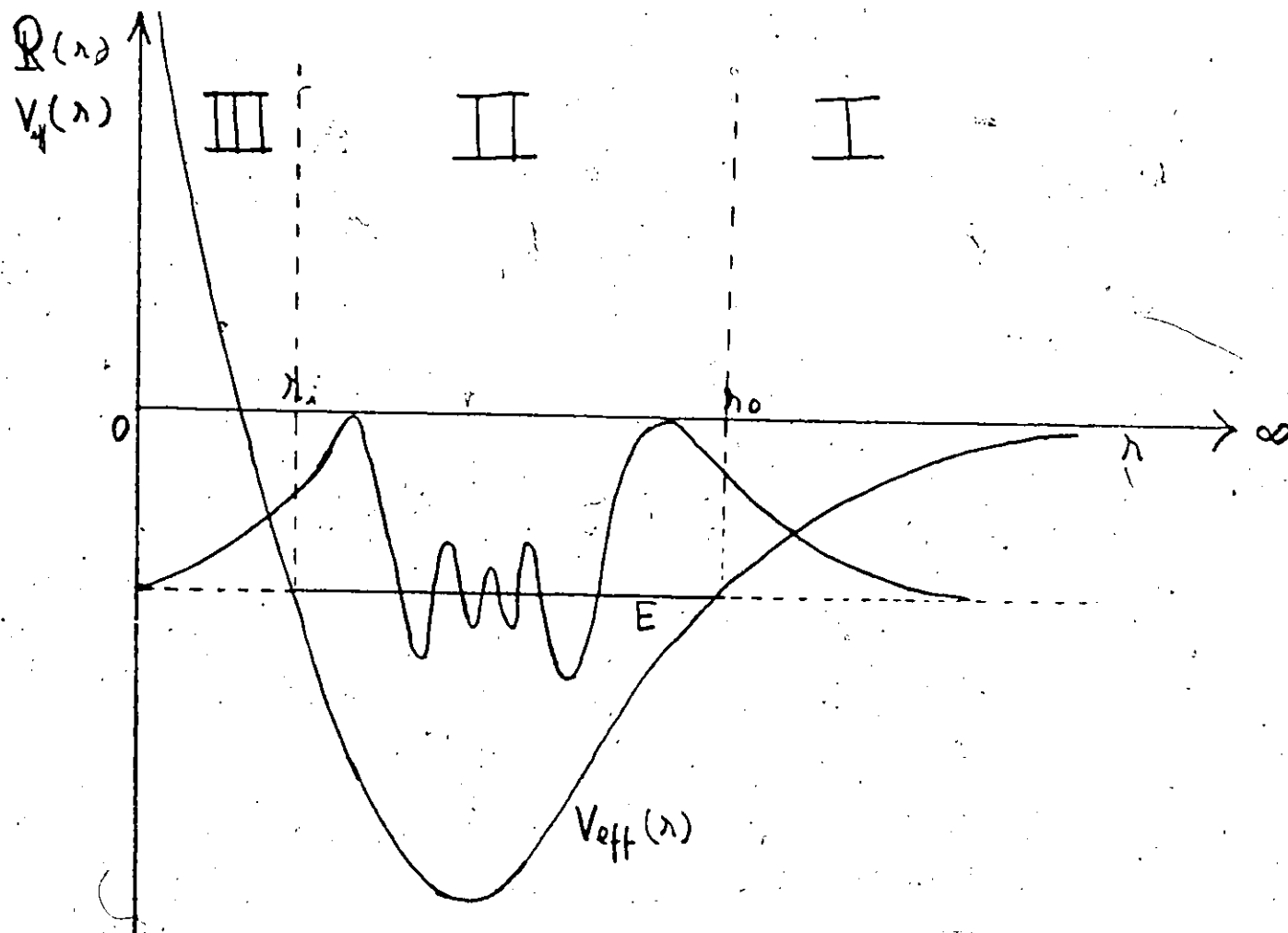


FIG. 1

r_1 and r_2 are the inner and the outer turning points respectively and are given by the two solutions of the equation (see the transformed Schroedinger Equation, Appendix C, previous report):

$$E = V_{eff}(r) + \frac{(l + \frac{1}{2})^2}{2r^2} \quad (25)$$

which are simply the two boundary points where the kinetic energy $[E - V_{eff}(r)]$ of the bound particle is zero. The kinetic energy is positive inside the well and negative outside in the forbidden regions I and III where the wave function decays exponentially.

As in the previous report on exchange pseudopotentials, we transform the radial Schroedinger equation to $y = \log r$ space and integrate from $-\infty$ inward, using Numerov's method, in order to obtain the radial wave function. The two required starting values for the wave function, are calculated from the Bates-Damgaard formula¹¹, which is valid in region I.

$$R_{nl}(x) = N^{-\frac{1}{2}} (2x)^{\nu} e^{-x} \sum_{t=0}^{t_{max}} \frac{C_+(t)}{t! (2x)^t} \quad (26)$$

where ν is the effective quantum number given by

$$\nu = n - \mu = Z/[2|E|]^{1/2}$$

and

$$x = 1Z/\nu$$

$$C_0(\nu) = 1$$

$$C_+(\nu) = C_{+1}(\nu) [l(l+1) - (\nu-t)(\nu-t+1)]$$

$$t_{max} = \text{Integral part of } (\nu + l + 2)$$

$$N = \frac{\nu^2}{Z} [\Gamma(\nu + l + 1) \Gamma(\nu - l)]$$

11. W. E. Baylis, JILA Report, No. 100 (Appendix A), 1969.

It should be noted that the Bates-Damgaard formula is an asymptotic expansion and therefore while doing the computations, care should be taken to ensure that the expansion parameter X is large enough so that the expression (26) does not diverge as $t \rightarrow t_{\max}$. Also in order to incorporate the effect of the polarization potential α_d/λ^4 on $R_{\nu\ell}$, we must modify the coefficients $C_+(\nu)_{\text{as}}$ ¹²:

$$C_+(\nu) = C_{+,-1} [(\nu-t+1)(\nu-t) - \ell(\ell+1)] \\ - (t-1)(t-2) \alpha_d \left(\frac{2}{\nu}\right)^2 C_{+,-3}$$

Eq. (24), then, ensures that the wave function starts out with the right asymptotic form. Then, region II, between the inner and the outer turning points, we constrain the wave function to have the right number of nodes $N (= n - \ell - 1)$. This is done by modifying the trial potential according to the following scheme based on the WKB method.

In the WKB approximation, the phase integral is given in terms of the number of nodes as follows:

$$\int_{y_1}^{y_2} k dy = (N + \frac{1}{2}) \pi \quad (27)$$

where

$$\text{and } k = \left\{ \left[2(E - V(\lambda)) \right] \lambda^2 - \left(\ell + \frac{1}{2} \right)^2 \right\}^{\frac{1}{2}} \quad (28)$$

Suppose now that the wave function $|i\rangle$ initially has N_i nodes then we want to change the potential (by varying α_i) such that the number of nodes is $(N_i - \ell_i - 1)$. We therefore calculate the rate of change of nodes with respect to α_i i.e.

12. W. E. Baylis, Private Communication.

$$\frac{\partial N_i}{\partial \alpha_i} = \frac{1}{\pi} \frac{\partial}{\partial \alpha_i} \int_{y_i}^{y_0} k_i dy \quad (29)$$

which from Eq. (28):

$$= -\frac{1}{\pi} \int_{y_i}^{y_0} \frac{y^2}{k_i} \left[\frac{\partial v}{\partial \alpha_i} \right] dy \quad (30)$$

Hence the change $\delta \alpha_i$ required to yield the right number of nodes N_i , is given by:

$$\delta \alpha_i = - [N_i' - N_i] / \left(\partial N_i / \partial \alpha_i \right) \quad (31)$$

where the denominator is calculated from Eq. (30).

Thus, before starting the main computing procedure, the potential is adjusted in the manner described above.[†]

Having thus constrained the behaviour of the wave function in regions III and II, we now have to adjust the parameter in the potential such that the wave function has the right behaviour in region I, i.e. as $\lambda \rightarrow 0$. This is the most important task involved in the present method.

If our potential is not exact then wave function obtained will, in general, be a linear combination of the regular and the irregular solutions of the Schroedinger equation, i.e.

[†] We may recall that Bottcher had used the Hartree-Fock potential (along with the polarization terms) as the starting potential. But since the H-F potential is calculated from the antisymmetrized wave function, it is rather tedious and time consuming to calculate. Comparably, our method is considerably easier and faster.

$$Q \quad R \underset{\lambda \rightarrow 0}{\sim} A \lambda^{l+1} + B \lambda^{-l} \quad (32)$$

The task therefore is to adjust the potential so as to eliminate the irregular solution which causes the wave function to blow-up instead of decaying exponentially in region I. Once again we make use of the WKB approximation.

We can write the wave function as:

$$\psi = \frac{A}{\sqrt{x}} e^{-\int x dy} + \frac{B}{\sqrt{x}} e^{+\int x dy} \quad (33)$$

where

$$x = [2(V-E)\lambda^2 + (l+\frac{1}{2})^2]^{\frac{1}{2}}$$

Note that x is real when $E < V(\lambda)$ as in region I. Hence:

$$\begin{aligned} \left[\frac{1}{x} \frac{d}{dy} (\sqrt{x} \psi) \right] + x \psi &= 2A e^{-\int x dy} \\ \left[\frac{1}{x} \frac{d}{dy} (\sqrt{x} \psi) \right] - x \psi &= -2B e^{+\int x dy} \end{aligned} \quad (34)$$

We now multiply these two and define a new quantity 'T':

$$\left[\frac{1}{x} \frac{d}{dy} (\sqrt{x} \psi) \right]^2 - x^2 \psi^2 = -4AB \equiv T \quad (35)$$

We want the coefficient 'B' of the irregular solution to vanish and from

(32) we see that $B = 0$ when $T = 0$.†

† The regular and the irregular solution of the transformed Schroedinger equation near the origin are $\lambda^{l+\frac{1}{2}}$ and $\lambda^{-l-\frac{1}{2}}$. If we consider only the regular solution then as $\lambda \rightarrow 0$, $P(\lambda) \rightarrow \lambda^{l+\frac{1}{2}}$ and

$$x \xrightarrow{\lambda \rightarrow 0} (l+\frac{1}{2})$$

Therefore, as in the WKB approximation, if the irregular solution is not present then

$$T \xrightarrow{\lambda \rightarrow 0} \left[\frac{(l+\frac{1}{2})^{\frac{1}{2}}}{(l+\frac{1}{2})} \frac{d}{dy} (e^{y(l+\frac{1}{2})}) \right]^2 - (l+\frac{1}{2})^2 e^{2y(l+\frac{1}{2})} = 0$$

Therefore we have to vary the potential such that the 'T' value for the given wave function goes to '0' as $\lambda \rightarrow 0$. The potential is varied through some parameter α_i and the required variation is given by:

$$\delta \alpha_i = [0 - T(\alpha_i)] / [\partial T / \partial \alpha_i] \quad (36)$$

where the quantity $(\partial T / \partial \alpha_i)$ can be calculated analytically (see Appendix B). The 'T' value for the particular wave function under consideration is required to converge to within 'E' of zero (where 'E' is some small quantity typically $\approx 10^{-8}$). We then calculate and compare the eigenenergies of the potential with the spectroscopic eigenenergies.

4. Calculations

In accordance with the theory and the algorithm given above, a computer program was written to carry out the calculation (flow chart is given in Appendix A). In addition to the steps outlined in the algorithm, the program has the following features.

1. The distribution of the wave functions of the various excited energy levels of the valence electron of an alkali atom, vary over a fairly wide range. The full integration mesh should therefore be large enough to include the widest distribution of the given set of wave functions while at the same time the effective range of integration should be suitably varied in each case depending upon the range of probability distribution of the particular wave function under consideration. We therefore choose a mesh (in log grid) which is large enough to cover the widest distribution but for each wave function, the starting point R_I for

inward integration is different and is taken to be equal to twice the outer turning point for that wave function. The potential $V(r)$ in the asymptotic region is given by $-\frac{\gamma}{\lambda}$, hence the outer turning point λ_0 is approximately given by:

$$E - V(\lambda) = 0 \quad (37)$$

$$-E \approx \gamma/\lambda_0 \quad (38)$$

hence

$$R_I = 2\lambda_0 \approx 2\gamma/|E| \quad (39)$$

2. Having adjusted the parameter for a given state such that $T < E$ (E was chosen to be 10^{-8}) and all other states remaining stationary, we calculate the eigenenergies of the potential for all states required to be fitted. We start with the experimental eigenvalue ' E ' and the potential $V(\lambda, \lambda)$ and calculate the wave function corresponding to ' E '. If the ' T ' value for that wave function is $< 10^{-8}$ then we change ' E ' by an amount δE which is given by:

$$\delta E = [0 - T] / (dT/dE) \quad (40)$$

The new ' T ' value will be closer to '0' than the previous one. This iteration procedure is continued until the eigenvalue ' E ' has been adjusted to the eigenvalue of the potential.

3. The program starts the computations from the parameters in the SR part of the potential which means that the LR part should initially be specified as well as possible. Otherwise in order to fit the lower few eigenstates, the program will try to modify the LR part by varying parameters in the SR part and this inevitably would lead to certain computational instabilities (mainly slow convergence or even divergence). The LR part is therefore initially fitted with the accepted values of the dipole and quadrupole polarizabilities and cut-off lengths. Also, if convergence for a given parameter is not achieved within a few iterations then the next parameter is altered slightly and the iteration process is started all over again.
4. We have chosen a potential with six parameters; three in the SR and LR part each i.e.

$$V(\alpha, \lambda) = - \left[\frac{(2-\beta)}{\lambda} e^{-\alpha_1 \lambda} (1 + \alpha_2 \lambda + \alpha_3 \lambda^2) + \frac{\frac{1}{2} \alpha_4 \lambda^2}{(\lambda^2 + \alpha_6)^3} + \frac{(\alpha_5 - 3\beta \alpha_6) \lambda^2}{(\lambda^2 + \alpha_4)^4} \right] \quad (41)$$

α_5 is initially equal to $\alpha_4 - 3\beta \alpha_6$.

5. During the course of the computations it was found that since the total effective potential includes the centrifugal potential $\frac{l(l+1)}{\lambda^2}$; it is numerically quite difficult to fit into the same potential the eigenenergies corresponding to different angular momenta, l . We therefore construct different potentials for different l series e.g. $l = 0; n = 1 \dots N$ and $l = 1; n = 1 \dots N'$ etc. Thus the total effective potential has the same shape for all 'n' states corresponding to a given l . The shape of the potential is varied, through the corresponding set of parameters, to approximate the real potential.

This method insures that the eigenfunction for any state $|n,l\rangle$ in the atom will be orthogonal to all other states as it should.

Calculations are carried out for different l series of Sodium and Potassium. Results and relevant data are given in the next section.

III. RESULTS AND DISCUSSION

The results consist of the final parameter for the potential (41) and the eigenenergies of the potential with those parameters. The experimental set of eigenenergies is also given for comparison. The experimental eigenenergies are taken from Risberg[†] (Ark. Physik. 10, 1956) and are the most accurate ones available. The mean experimental error is given to be 0.03 cm^{-1} i.e. approximately $O(10^{-7})$ Hartrees. In the following tables we have used atomic units throughout.

The spin-orbit potential is not included in the calculations reported.

1.

SODIUM

Atomic Number (Z) = 11

Core Charge (z) = 1

Dipole Polarizability (Core) = 0.9459*

Potential for 'nS' States of Na

$$\alpha_1 = 2.9550576$$

$$\alpha_2 = -1.7784792$$

$$\alpha_3 = 3.0$$

$$\alpha_4 = 0.4$$

$$\alpha_5 = -0.5$$

$$\alpha_6 = 0.36$$

[†] V. B. Sheorey, Private Communication.

* J. G. Weisheit and A. Dalgarno (1969).

	EXPERIMENTAL EIGENENERGIES	EIGENENERGIES OF THE POTENTIAL
3S	0.1888620	0.1888620
4S	0.07157922	0.07157921
5S	0.03758503	0.03758613
6S	0.02313225	0.02313312
7S	0.01566230	0.01566297
8S	0.01130422	0.01130476
9S	0.008541465	0.008541959
10S	0.006680520	0.006681033
11S	0.005367765	0.005368188
12S	0.004407085	0.004407547

Potential for 'nP' States of Na

$$\alpha_1 = 2.6358296$$

$$\alpha_2 = -1.2329905$$

$$\alpha_3 = 2.3800125$$

$$\alpha_4 = 0.8999545$$

$$\alpha_5 = 0.7615$$

$$\alpha_6 = 0.8$$

	EXPERIMENTAL EIGENENERGIES	EIGENENERGIES OF THE POTENTIAL
3P	0.111504	0.111504
4P	0.05093627	0.05093627
5P	0.02919548	0.02919547
6P	0.01891978	0.01891976
7P	0.01325374	0.01325386
8P	0.0097999	0.009800089

Potential for 'nD' States of Na

$$\alpha_1 = 3.619439$$


$$\alpha_2 = -0.87540$$

$$\alpha_3 = 3.0210$$

$$\alpha_4 = 0.8$$

$$\alpha_5 = 0.7615$$

$$\alpha_6 = 0.8$$



	EXPERIMENTAL EIGENENERGIES	EIGENENERGIES OF THE POTENTIAL
3D	0.0559375	0.0559375
4D	0.03144274	0.03144521
5D	0.02010613	0.02010818
6D	0.01395265	0.01395413
7D	0.01024521	0.01024622
8D	0.00784045	0.007841243
9D	0.0061928	0.00619334
10D	0.00501486	0.005015179
11D	0.00414349	0.00414384

2.0

POTASSIUM

Atomic Number (Z) = 19

Core Charge (Z) = 1

Dipole Polarizability = 5.331*

Potential for 'nS' States of K

$$\alpha_1 = 2.2673939$$

$$\alpha_2 = 0.81954939$$

* J. C. Weisheit and A. Dalgarno (1969).

$$\alpha_3 = 1.0$$

$$\alpha_4 = 1.0$$

$$\alpha_5 = 0.8$$

$$\alpha_6 = 1.0$$

	EXPERIMENTAL EIGENENERGIES	EIGENENERGIES OF THE POTENTIAL
4S	0.1595185	0.1595185
5S	0.06371299	0.06371300
6S	0.03444218	0.03444285
7S	0.02157678	0.02157742
8S	0.01478278	0.01478334
9S	0.01075957	0.01076012
10S	0.00818124	0.008181771
11S	0.00643013	0.006430632
12S	0.0051866	0.005187159
13S	0.00427135	0.004272485

Potential for 'nP' States of K

$$\alpha_1 = 1.9547053$$

$$\alpha_2 = -1.0963235$$

$$\alpha_3 = 0.85105432$$

$$\alpha_4 = 1.0$$

$$\alpha_5 = 0.8$$

$$\alpha_6 = 1.0$$

	EXPERIMENTAL EIGENENERGIES	EIGENENERGIES OF THE POTENTIAL
4P	0.1001885	0.1001885
5P	0.04691552	0.04691552
6P	0.02736217	0.02736215
7P	0.01794333	0.01793890
8P	0.0126698	0.01267001
9P	0.00942481	0.009425184
10P	0.00728481	0.007285226

As seen above the results given above are in good agreement with the experimental values. The mean error in the experimental values is $0(10^{-7})$ Hartrees. We expect the error to be less than the mean for the lower states and higher for states high up in the spectrum. Accordingly if we examine the calculated values we find that these values are approximately within experimental error.

In our program we evaluate the 'T' value at approximately $1/(16 \cdot Z)$ bohrs (≥ 0.005 for Sodium) and we expect that at this point we have gone far in enough from the inner turning point for the WKB approximation to be valid ('T' is calculated from WKB method).

We have found that the following relation (see Appendix B) is valid for a fairly large range of values of 'T':

$$\Delta T = 4 \cdot \Delta E \quad (42)$$

Eq. (42) can therefore be used to find the eigenvalues of the potential.

At present we are attempting to determine the best possible expression for 'T' and the point 'r' where it should be evaluated. Also we shall attempt to check our model potential by conducting independent tests like calculating the oscillator strengths for the wave functions obtained from the potential.

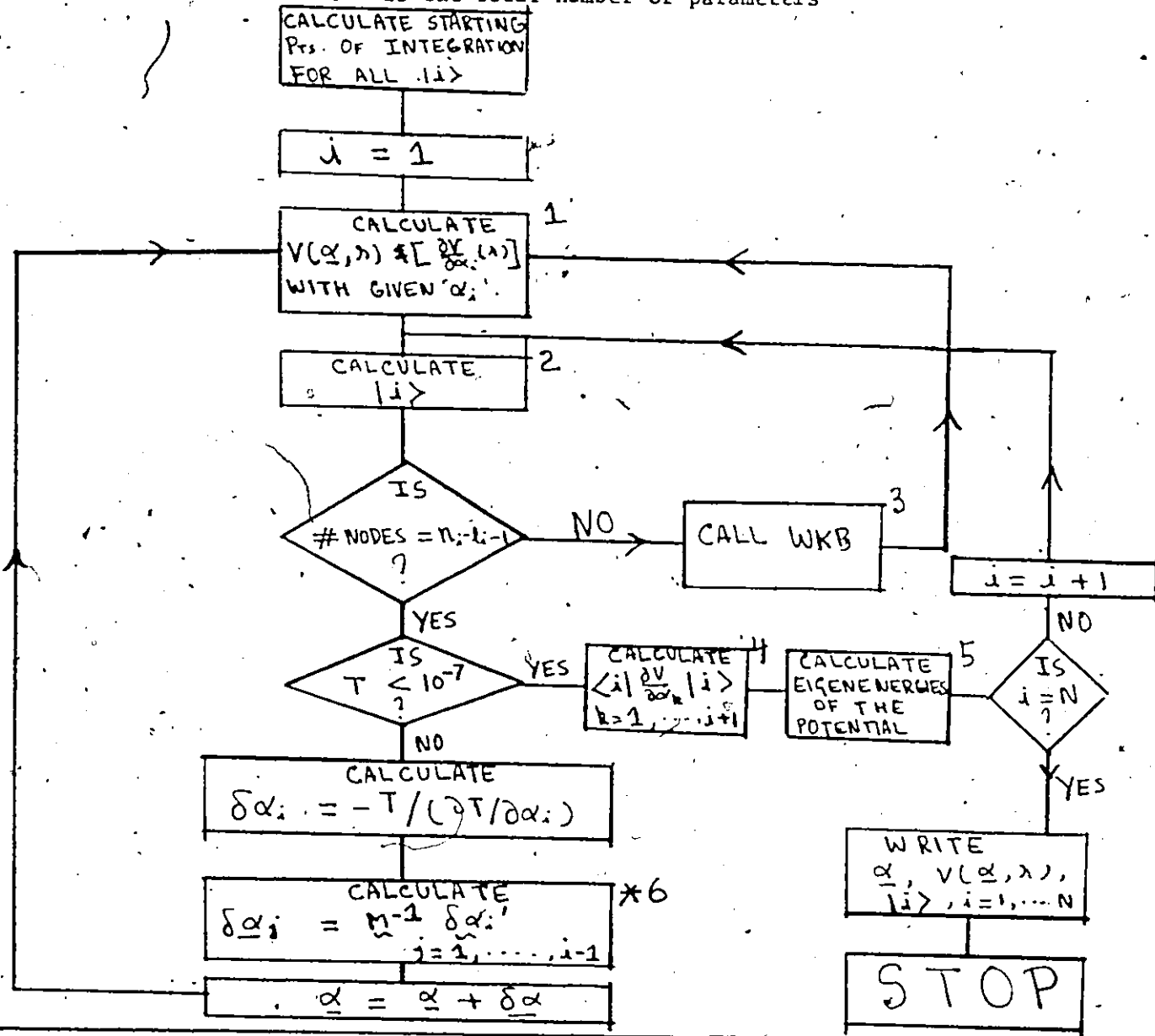
At this stage we can conclude from the preliminary results given above that our computer program is capable of constructing a model potential by adjusting at least up to 4 parameters in the parametrized form to fit exactly the corresponding number of eigenstates. The rest of the eigenstates in a given 'J' series should also be obtained within experimental accuracy.

APPENDIX A

Flow Chart for the Main Program.

The following is a very brief outline of the main program simply mentioning the basic steps of the calculations.

where N is the total number of parameters



$$* \underline{M} = \begin{bmatrix} \langle i | \frac{\partial V}{\partial \alpha_i} | i \rangle & \dots & \langle i | \frac{\partial V}{\partial \alpha_{i-1}} | i \rangle \\ \vdots & & \vdots \\ \langle i-1 | \frac{\partial V}{\partial \alpha_i} | i-1 \rangle & \dots & \langle i-1 | \frac{\partial V}{\partial \alpha_{i-1}} | i-1 \rangle \end{bmatrix}$$

$$\delta \alpha_i = \delta \alpha_i \begin{bmatrix} \langle i | \frac{\partial V}{\partial \alpha_i} | i \rangle \\ \vdots \\ \langle i-1 | \frac{\partial V}{\partial \alpha_i} | i-1 \rangle \end{bmatrix}$$

1. Subprogram POT calculates the potential and derivatives w.r.t. α each time the parameter vector $\delta\alpha$ is changed.
2. Subroutine WFCN solves the transformed radial Schroedinger equation to calculate the radial wave function $P_{n\ell} = \frac{R_{n\ell}}{r}$ using Numerov's method starting with Bates-Damgaard ~~type~~ functions.
3. Subroutine WKB calculates the change in α_i required to make the phase integral $\int_{y_i} k_i dy = (n_i - \ell_i - \frac{1}{2})\pi$
4. Subprogram MAT calculates the matrix elements $\langle R_i | \frac{\partial V}{\partial \alpha_k} | R_i \rangle$ using the Double Simpson's integration method. The actual matrix elements used in calculation of $\delta\alpha_i$ are $\langle R_i | \frac{\partial V}{\partial \alpha_k} | R_i \rangle / \langle R_i | R_i \rangle$
5. Subroutine EIGEN calculates the eigenenergies of the potential using the 'T' value as the test criterion. Simple variation-iteration procedure is used.
6. Section GEJ of subprogram WKB solves this matrix equation and calculates the $\delta\alpha_i$ using Gauss-Jordan elimination procedure.

APPENDIX B

Analytical Calculation of ΔT for Small Perturbation ΔV

We can rewrite Eq. (35) for 'T' as:

$$\begin{aligned}
 T &= \frac{1}{x} \left\{ \left[\psi' + \frac{(x^2)'}{4x^2} \psi \right]^2 - x^2 \psi^2 \right\} \\
 &= f^{-1/2} \left\{ \left[\psi' + \frac{f'}{4f} \psi \right]^2 - f \psi^2 \right\} \\
 &= f^{-5/2} \left\{ \left[f \psi' + \frac{f'}{4} \psi \right]^2 - f^3 \psi^2 \right\} \quad (1)
 \end{aligned}$$

where $f = x^2$

We know that:

$$\psi'' = f \psi \quad (2)$$

$$\psi'' + \delta \psi'' = (f + \delta f)(\psi + \delta \psi) \quad (3)$$

For (2) and (3)

$$\delta \psi'' = (f + \delta f) \delta \psi + (\delta f) \psi \quad (4)$$

Subtracting $\delta \psi$ (2) from ψ (4):

$$\begin{aligned}
 \psi \delta \psi'' - (\delta \psi) \psi'' &= \psi (f + \delta f) \delta \psi + \psi (\delta f) \psi - (\delta \psi) f \psi \\
 &= \psi (\delta f) \psi + \psi (\delta f) \delta \psi \\
 &= \frac{d}{dy} [\psi \delta \psi' - (\delta \psi) \psi'] \quad (5)
 \end{aligned}$$

But since $[\psi \delta \psi' - (\delta \psi) \psi'] = 0$ at $y = \infty$

$$\therefore \psi \delta \psi' - (\delta \psi) \psi' = - \int_0^{\infty} dy' [\psi \delta f (\psi + \delta \psi)] \quad (6)$$

Now as $\lambda \rightarrow 0$; $x \rightarrow (x + \frac{1}{2})$

$$T = \frac{1}{(x + \frac{1}{2})} [\psi'^2 - x^2 \psi^2] \quad (7)$$

and

$$\delta T = \frac{2}{(x + \frac{1}{2})} [\psi' \delta \psi' - x^2 \psi \delta \psi] \quad (8)$$

At $T = 0$, $\psi' = x \psi$

$$\delta T = 2 [\psi \delta \psi' - \psi' \delta \psi] = -2 \int_0^{\infty} y' [\psi \delta f (\psi + \delta \psi)] \quad (9)$$

which in first order is:

$$= -2 \langle R_i | \frac{\partial f}{\partial x^2} | R_i \rangle \quad (10)$$

i.e.

$$\Delta T = -4 \langle R_i | \Delta V | R_i \rangle \quad (11)$$

Eq. (11) enables us to calculate T and $T + \Delta T$, corresponding to α_i and $\alpha_i + \Delta \alpha_i$, for a given wave function $|R_i\rangle$. We can also use Eq. (11) instead of Eq. (40), for calculating the eigenenergies of an arbitrary potential.

VITA-AUCTORIS

I was born on July 26, 1951 in Fatehgarh, India. After graduating from Central Higher Secondary School in Kanpur, Uttar Pradesh in 1968, I moved to Calgary, Alberta with my parents and joined the University of Calgary and completed the first two years of my Bachelors. I then moved to Windsor, again with my parents, and obtained the Bachelors degree in Honours Physics from the University of Windsor in 1972.

I subsequently enrolled in the Masters program at the same university.